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The rotational excitation of molecules

4.1 Introduction

The quantum theory of molecular collisions has been extensively developed over the last three decades. As in many branches of theoretical science, the growth of this subject has been closely linked with the advances in computer technology. Powerful numerical techniques have been developed for solving Schrödinger's equation, which are well adapted to low energy, molecular collision problems, at various levels of approximation. A basic reference text in this context is *Atomic, Molecular and Optical Physics Handbook* [43]. The complexity of the problems that can be tackled, and the accuracy of the results that can be obtained, continue to be determined by the available computing power.

Any proper discussion of molecular collision processes involves the concept of the potential energy curve or surface. This concept drives from the Born–Oppenheimer approximation, to which we first turn.

4.2 The Born–Oppenheimer approximation

For the sake of simplicity, when discussing the basic concepts, we consider the collision between a one-electron atom, A, and a fully-stripped ion, B. The theory which pertains to this illustrative case can be generalized to collisions between many-electron atoms or to collisions between molecules.

When studying a collision problem, we are interested in the relative motions of the particles involved, and not in the motion of the centre of mass (*barycentre*) of the colliding system. The velocity of the centre of mass remains constant and is irrelevant to the scattering processes to which we progress below. The position of the centre of mass, relative to a space-fixed or laboratory reference frame, will be denoted by \mathbf{R}_C and the coordinates of the centre of mass of A and of B by \mathbf{R}_A and \mathbf{R}_B , respectively. \mathbf{R} is the vector connecting the centre of mass of A to B and is taken to be directed from A to B; see Fig. 4.1. The position of the centre of mass of the system is defined such that

$$\begin{aligned}\mathbf{R} &= \mathbf{R}_{AC} + \mathbf{R}_{CB} \\ &= \frac{m_B}{m_A + m_B} \mathbf{R} + \frac{m_A}{m_A + m_B} \mathbf{R}\end{aligned}\tag{4.1}$$

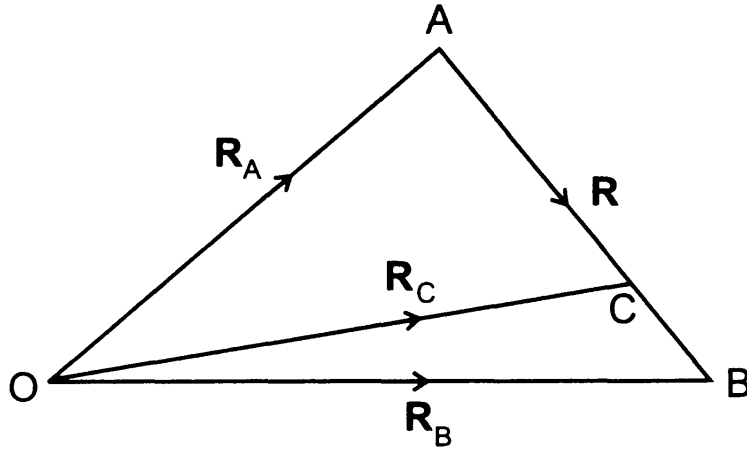


Figure 4.1 Defining the space-fixed or laboratory coordinates of an atom, A, and a fully-stripped ion, B, and of their centre of mass, C; the relative coordinate, \mathbf{R} , is directed from A to B.

and the momentum of the system is

$$\begin{aligned}
 m_A \dot{\mathbf{R}}_A + m_B \dot{\mathbf{R}}_B \\
 &= m_A (\dot{\mathbf{R}}_C - \dot{\mathbf{R}}_{AC}) + m_B (\dot{\mathbf{R}}_C + \dot{\mathbf{R}}_{CB}) \\
 &= (m_A + m_B) \dot{\mathbf{R}}_C
 \end{aligned} \tag{4.2}$$

where use has been made of equation (4.1). Thus, the momentum of the system may be considered as being due to the total mass, $(m_A + m_B)$, located at the centre of mass.

Consider now the kinetic energy of the system,

$$\begin{aligned}
 \frac{1}{2} m_A \dot{\mathbf{R}}_A^2 + \frac{1}{2} m_B \dot{\mathbf{R}}_B^2 \\
 &= \frac{1}{2} m_A (\dot{\mathbf{R}}_C - \dot{\mathbf{R}}_{AC})^2 + \frac{1}{2} m_B (\dot{\mathbf{R}}_C + \dot{\mathbf{R}}_{CB})^2 \\
 &= \frac{1}{2} (m_A + m_B) \dot{\mathbf{R}}_C^2 + \frac{1}{2} \mu \dot{\mathbf{R}}^2
 \end{aligned} \tag{4.3}$$

where $\mu = m_A m_B / (m_A + m_B)$ is the *reduced mass* of the system. Thus, the kinetic energy comprises contributions from the total mass, moving with the velocity of the centre of mass, $\dot{\mathbf{R}}_C$, and from the reduced mass, moving with the relative velocity, $\dot{\mathbf{R}}$, of A and B. When the system is isolated, as we assume, the velocity of the centre of mass is constant and may be removed by a change of inertial frame; there remains the relative kinetic energy, which is available for exciting the internal degrees of freedom of the colliding system. Thus, we may consider the atom A to move with reduced mass, μ , relative to a fixed centre of force, B.

When discussing the interactions between atoms and molecules, it is often convenient to use the atomic system of units, in which $e = m_e = \hbar = 1$. In these units, the hamiltonian of the system AB may be written

$$H(\mathbf{x}, \mathbf{R}) = H_A(\mathbf{x}, \mathbf{R}) - \frac{\nabla_R^2}{2\mu} + V(\mathbf{x}, \mathbf{R}) \tag{4.4}$$

where \mathbf{x} is the position vector of the electron with respect to the centre of mass of A and B, $H_A(\mathbf{x}, \mathbf{R})$ represents the electronic hamiltonian of the atom A and $V(\mathbf{x}, \mathbf{R})$ is the potential of interaction between A and B; $-\nabla_R^2/(2\mu)$ is the relative kinetic energy operator, and ∇^2 the Laplacian operator ($\nabla_R^2 = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}$). Our task is to solve the Schrödinger equation

$$H\Psi = E\Psi \quad (4.5)$$

where E is the total barycentric energy of the colliding system, which is the kinetic energy of relative motion of A and B at infinite separation. The wave function is $\Psi = \Psi(\mathbf{x}, \mathbf{R})$.

Let us write the wave function in the following form, which retains generality but hints at the separation of the dependences on the electronic coordinates, \mathbf{x} , and the relative coordinates, \mathbf{R} :

$$\Psi(\mathbf{x}, \mathbf{R}) = \sum_i F_i(\mathbf{R})\phi_i(\mathbf{x}, \mathbf{R}) \quad (4.6)$$

For fixed R , equation (4.6) is an expansion of the wave function in terms of the solutions of the wave equation

$$[H_A(\mathbf{x}, \mathbf{R}) + V(\mathbf{x}, \mathbf{R})]\phi_i(\mathbf{x}, \mathbf{R}) = E_i(\mathbf{R})\phi_i(\mathbf{x}, \mathbf{R}) \quad (4.7)$$

which form an orthonormal (orthogonal and normalized) set of functions, such that

$$\langle \phi_j | \phi_i \rangle = \int \phi_j^*(\mathbf{x}, \mathbf{R})\phi_i(\mathbf{x}, \mathbf{R}) d\mathbf{x} = \delta_{ij} \quad (4.8)$$

where δ_{ij} is the Kronecker delta symbol ($\delta_{ij} = 1$ if $i = j$, $\delta_{ij} = 0$ if $i \neq j$). Substituting (4.6) in the Schrödinger equation (4.5) and projecting out ϕ_j by operating with $\int d\mathbf{x} \phi_j^*(\mathbf{x}, \mathbf{R})$ on both sides of the equation, we obtain

$$\begin{aligned} & \left[-\frac{\nabla_R^2}{2\mu} + E_j(\mathbf{R}) - E \right] F_j(\mathbf{R}) \\ &= \sum_i \left[\frac{\langle \phi_j | \nabla \mathbf{R} | \phi_i \rangle \cdot \nabla \mathbf{R} F_i(\mathbf{R})}{\mu} + \frac{\langle \phi_j | \nabla_R^2 | \phi_i \rangle F_i(\mathbf{R})}{2\mu} \right] \end{aligned} \quad (4.9)$$

Were it not for the terms on the right-hand side of equation (4.9), we would have succeeded in separating Schrödinger's equation into (4.7) for the electronic motion at a given value of \mathbf{R} , and (4.9) for the relative motion on a given *electronic potential energy surface*, $E_j(\mathbf{R})$.

The approximation of neglecting the coupling between the electronic and relative motions, embodied in the terms on the right-hand side of (4.9), is known as the 'adiabatic' or Born–Oppenheimer approximation. These terms give rise to transitions between potential energy curves, are responsible for charge transfer processes (Chapter 8), and can be responsible for fine structure transitions in atoms and ions (Chapter 6), induced in collisions with other atomic or molecular species. In the discussion of rotational excitation processes which follows, the collision will be assumed to take place along a single adiabatic potential energy curve.

4.3 The scattering of an atom by a rigid rotator

The theory of the scattering of a structureless particle by a rigid rotator (rotor) was given its first quantum mechanical formulation by Arthurs and Dalgarno [44]. Their approach is applicable to collisions between any particle without internal structure, or whose internal structure may be neglected, and a two-particle system possessing internal angular momentum. The degrees of freedom of such a system may be defined by the three polar coordinates of the atom A in a coordinate system whose origin is at the centre of mass M of the rotor BC and which is fixed in space, together with the two polar angles defining the orientation of BC in this same coordinate frame. The atom may be considered to move with reduced mass $\mu = m_A(m_B + m_C)/(m_A + m_B + m_C)$ relative to the centre of mass of the rotor.

An alternative approach [45] is to define the polar angles of BC relative to a coordinate system in which the Z-axis coincides with MA and rotates in space in the course of the collision. This 'body-fixed' frame of reference is the more natural choice from the viewpoint of the interaction potential, which depends on R and θ' only; see Fig. 4.2. However, as B and C are now moving relative to a coordinate system which is itself rotating, Coriolis forces arise, in addition to centrifugal forces. We shall consider the relative merits of these two coordinate frames in the discussion below.

An interesting analogy may be drawn between atom–rigid rotor scattering, as formulated by Arthurs and Dalgarno [44], and e^- –H scattering, as formulated by Percival and Seaton [46] and considered in Chapter 9. If electron exchange is neglected, the two problems become formally very similar. Indeed, as we shall see below, the algebraic coefficients that arise in the quantum mechanical treatment of atom–rigid rotor scattering are identical to coefficients tabulated by Percival and Seaton.

Let us denote by (Θ, Φ) the orientation of the body-fixed (BF) Z-axis relative to the space-fixed (SF) frame, xyz . The polar coordinates of particle A in the SF frame are then

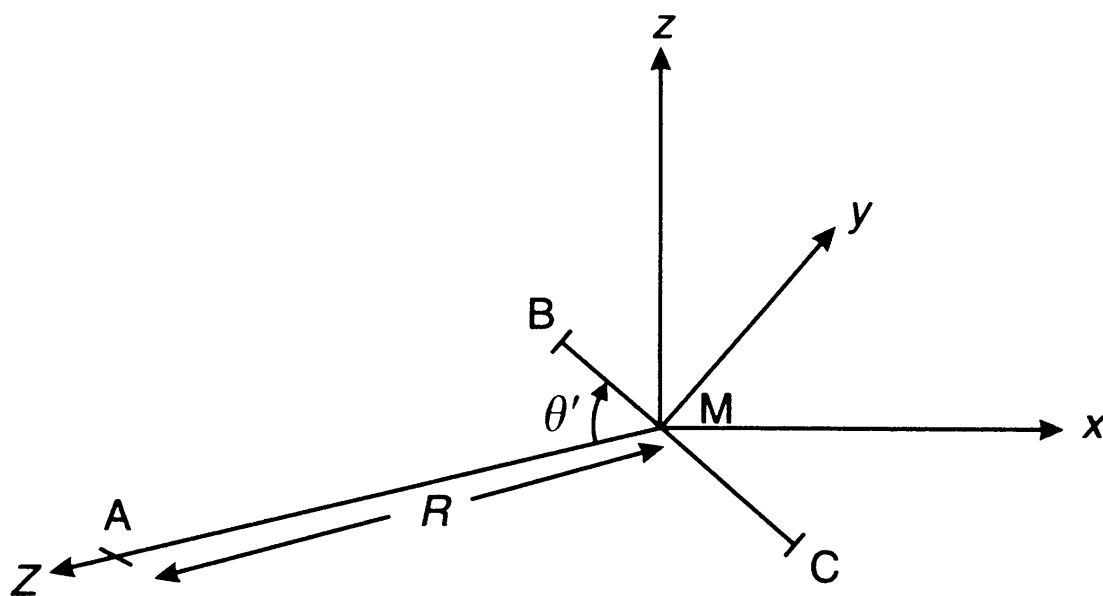


Figure 4.2 Defining the space-fixed coordinate system xyz and the body-fixed Z-axis for the collision between an atom A and a rigid rotor BC, whose centre of mass is M; R and θ' are sometimes called 'Jacobi coordinates'.

(R, Θ, Φ) . As noted above, the polar angles of BC may be expressed relative to either the SF or the BF frame. Let us denote these angles (θ, ϕ) and (θ', ϕ') , respectively.

Calculations are facilitated by expressing the wave function of the rotor in terms of a complete set of orthonormal functions of the polar angles (θ, ϕ) or (θ', ϕ') . The normalized spherical harmonics, Y , form such a set of functions. Denoting the angular momentum quantum number of the rotor by j and its projection on the SF z -axis by m , we have that

$$Y_{jm}(\theta, \phi) = (-1)^m \left[\frac{(2j+1)(l-m)!}{4\pi(l+m)!} \right]^{\frac{1}{2}} P_j^m(\cos \theta) e^{im\phi}, \quad (m \geq 0) \quad (4.10)$$

with

$$Y_{j,-m}(\theta, \phi) = (-1)^m Y_{jm}^*(\theta, \phi) \quad (4.11)$$

and where $P_j^m(\cos \theta)$ is an associated Legendre polynomial [47]. In the BF coordinate system, the corresponding set of functions is $Y_{j\Omega}(\theta', \phi')$, where Ω is the projection of \mathbf{j} , the angular momentum of the rotor, on the BF Z -axis. In order to establish the relationship between $Y_{jm}(\theta, \phi)$ and $Y_{j\Omega}(\theta', \phi')$, it is necessary to introduce the concepts of the *Euler angles* and the *rotation matrix*, \mathbf{D} .

The Euler angles (α, β, γ) define a sequence of three rotations, successively through α about the z -axis, through β about the new y -axis, and through γ about the new z -axis, which takes the SF coordinate system into the BF system. The rotations are taken in the positive sense, that is, in the sense of inserting a right-handed screw. In the example that we are considering, it may be verified that the Euler angles are $\alpha = \Phi$, $\beta = \Theta$, and γ is arbitrary, usually taken to be zero. The elements of the rotation matrix, \mathbf{D} , are defined by Rose [48] and Brink and Satchler [49] as

$$D_{m'm}^j(\alpha, \beta, \gamma) = \langle jm' | e^{-i\alpha j_z} e^{-i\beta j_y} e^{-i\gamma j_z} | jm \rangle \quad (4.12)$$

where $|jm\rangle = Y_{jm}(\theta, \phi)$ and j_z, j_y are components of the angular momentum operator in the SF system, where

$$j_x^2 + j_y^2 + j_z^2 = \mathbf{j}^2 \quad (4.13)$$

Using the quantum theory of angular momentum, (4.12) may be written

$$D_{m'm}^j(\alpha, \beta, \gamma) = e^{-im'\alpha} d_{m'm}^j(\beta) e^{-im\gamma} \quad (4.14)$$

where

$$d_{m'm}^j(\beta) = \langle jm' | e^{-i\beta j_y} | jm \rangle \quad (4.15)$$

Explicit expressions for $d_{m'm}^j(\beta)$ are given by Rose [48] and Brink and Satchler [49]. In another standard text on angular momentum theory, Edmonds [50] defines a rotation matrix \mathcal{D} whose elements relate to Rose and Brink and Satchler through

$$\mathcal{D}_{m'm}^j(\alpha, \beta, \gamma) = D_{mm'}^{j*}(\alpha, \beta, \gamma) \quad (4.16)$$

Thus, \mathcal{D} is the transposed complex conjugate of \mathbf{D} . Either of these conventions may be adopted but must be adhered to. We shall adopt the definition (4.12) of Rose and Brink and Satchler, in which case

$$Y_{jm}(\theta, \phi) = \sum_{\Omega} D_{m\Omega}^{j*}(\Phi, \Theta, 0) Y_{j\Omega}(\theta', \phi') \quad (4.17)$$

and the inverse relation

$$Y_{j\Omega}(\theta', \phi') = \sum_m D_{m\Omega}^j(\Phi, \Theta, 0) Y_{jm}(\theta, \phi) \quad (4.18)$$

apply. The functions (4.17) are eigenfunctions of \mathbf{j}^2 and j_z , with eigenvalues $j(j+1)$ and m , respectively, whereas the functions (4.18) are eigenfunctions of \mathbf{j}^2 and j_z , with eigenvalues $j(j+1)$ and Ω .

Conservation laws are at the heart of physics, and it is advantageous, when solving a dynamical problem, to make use of the fact that the total angular momentum is conserved. This symmetry property arises from the invariance of the hamiltonian describing the dynamical system under rotations of the system in space. Put in other words, the orientation of the SF coordinate system may be chosen arbitrarily. In the problem under consideration, the total angular momentum, \mathbf{J} , is composed of the angular momentum of the rotor, \mathbf{j} , and the angular momentum of the atom relative to the rotor, \mathbf{l} :

$$\mathbf{J} = \mathbf{j} + \mathbf{l}$$

$$J_z = j_z + l_z$$

Eigenfunctions of \mathbf{j}^2 and j_z have already been given as $Y_{jm}(\theta, \phi)$. Similarly, the eigenfunctions of \mathbf{l}^2 and l_z are $Y_{lm_l}(\Theta, \Phi)$, with eigenvalues $l(l+1)$ and m_l , respectively. It follows that the product $Y_{jm}(\theta, \phi) Y_{lm_l}(\Theta, \Phi)$ is an eigenfunction of $\mathbf{j}^2, j_z, \mathbf{l}^2$ and l_z , but it is *not* an eigenfunction of the total angular momentum operators \mathbf{J}^2 or J_z . However, such functions are readily formed as

$$\mathcal{Y}_{jJM}(\theta, \phi; \Theta, \Phi) = \sum_{mm_l} C_{mm_lM}^{j l J} Y_{jm}(\theta, \phi) Y_{lm_l}(\Theta, \Phi) \quad (4.19)$$

where $M = m + m_l$ and $C_{mm_lM}^{j l J}$ is a *Clebsch–Gordan coefficient*, which is related to the Wigner 3j-symbol through

$$C_{mm_lM}^{j l J} = (-1)^{j-l+M} (2J+1)^{\frac{1}{2}} \begin{pmatrix} j & l & J \\ m & m_l & -M \end{pmatrix} \quad (4.20)$$

[51]. Using equation (4.17) and the following relationship between a spherical harmonic and an element of the rotation matrix

$$Y_{lm_l}(\Theta, \Phi) = \left(\frac{2l+1}{4\pi} \right)^{\frac{1}{2}} D_{m_l 0}^{l*}(\Phi, \Theta, 0) \quad (4.21)$$

the eigenfunctions (4.19) may be expressed as

$$\begin{aligned} \mathcal{Y}_{jIJM}(\theta, \phi; \Theta, \Phi) &= \left(\frac{2l+1}{4\pi} \right)^{\frac{1}{2}} \sum_{\substack{mm_l \\ \Omega}} C_{mm_l M}^{jIJ} Y_{j\Omega}(\theta', \phi') \\ &\times D_{m\Omega}^{j*}(\Phi, \Theta, 0) D_{m_l 0}^{l*}(\Phi, \Theta, 0) \end{aligned} \quad (4.22)$$

The Clebsch–Gordan series [48] tells us that

$$D_{m\Omega}^j(\Phi, \Theta, 0) D_{m_l 0}^l(\Phi, \Theta, 0) = \sum_{J'} C_{mm_l M}^{jIJ'} C_{\Omega 0 \Omega}^{jIJ'} D_{M \Omega}^{J'}(\Phi, \Theta, 0) \quad (4.23)$$

and, as the Clebsch–Gordan coefficients are real, equation (4.22) becomes

$$\begin{aligned} \mathcal{Y}_{jIJM}(\theta, \phi; \Theta, \Phi) &= \left(\frac{2l+1}{4\pi} \right)^{\frac{1}{2}} \sum_{\substack{mm_l \\ J' \Omega}} C_{mm_l M}^{jIJ} C_{mm_l M}^{jIJ'} C_{\Omega 0 \Omega}^{jIJ'} \\ &\times Y_{j\Omega}(\theta', \phi') D_{M \Omega}^{J'*}(\Phi, \Theta, 0) \end{aligned} \quad (4.24)$$

The Clebsch–Gordan coefficients satisfy orthonormality relations [51], one of which is

$$\sum_{mm_l} C_{mm_l M}^{jIJ} C_{mm_l M'}^{jIJ'} = \delta_{JJ'} \delta_{MM'} \quad (4.25)$$

and so equation (4.24) reduces to

$$\mathcal{Y}_{jIJM}(\theta, \phi; \Theta, \Phi) = \left(\frac{2l+1}{2J+1} \right)^{\frac{1}{2}} \sum_{\Omega} C_{\Omega 0 \Omega}^{jIJ} \mathcal{Z}_{j\Omega JM}(\theta', \phi'; \Theta, \Phi) \quad (4.26)$$

where

$$\mathcal{Z}_{j\Omega JM}(\theta', \phi'; \Theta, \Phi) = \left(\frac{2J+1}{4\pi} \right)^{\frac{1}{2}} D_{M \Omega}^{J*}(\Phi, \Theta, 0) Y_{j\Omega}(\theta', \phi') \quad (4.27)$$

is an eigenfunction of \mathbf{J}^2 and J_Z . Equation (4.26) specifies the unitary transformation which relates the eigenfunctions of \mathbf{J}^2 in the SF frame, $\mathcal{Y}_{jIJM}(\theta, \phi; \Theta, \Phi)$, to the corresponding eigenfunctions in the BF frame, $\mathcal{Z}_{j\Omega JM}(\theta', \phi'; \Theta, \Phi)$. An alternative and more compact way of writing equation (4.26) is

$$|jIJM\rangle = |j\Omega JM\rangle \langle j\Omega JM | jIJM\rangle \quad (4.28)$$

with an implied summation over the index Ω , and where

$$\langle j\Omega JM | jIJM\rangle = \left(\frac{2l+1}{2J+1} \right)^{\frac{1}{2}} C_{\Omega 0 \Omega}^{jIJ} \quad (4.29)$$

is seen to be independent of the projection quantum number, $M = m + m_l$.

Equation (4.26), or its alternative form, equation (4.28), is an important result, enabling quantities evaluated in the rotating (BF) frame, which is more natural for expressing the interaction between A and BC, to be transformed into the laboratory (SF) frame, in which measurements are made. Note that, as the BF Z-axis is taken to be coincident with MA, the projection of the orbital angular momentum \mathbf{l} of A relative to BC on this axis is zero, as \mathbf{l} is perpendicular to MA. It follows that $j_Z = J_Z$. These facts are embodied in the Clebsch–Gordan coefficient, $C_{\Omega 0 \Omega}^{j l J}$, which appears in equation (4.29): the same projection quantum number, Ω , is associated with both j and J .

Another conservation law which may be used is associated with the parity of the eigenfunctions representing the system A + BC. The corresponding symmetry operation is the inversion of the coordinates of all particles (A, B and C) in the origin of the SF coordinate frame. The hamiltonian is invariant under this operation; the corresponding operator, P , gives rise to the following transformation of SF coordinates:

$$\begin{aligned}\theta &\rightarrow \pi - \theta, \phi \rightarrow \pi + \phi \\ \Theta &\rightarrow \pi - \Theta, \Phi \rightarrow \pi + \Phi\end{aligned}$$

Under this same operation, the BF coordinates transform as

$$\theta' \rightarrow \theta', \phi' \rightarrow \pi - \phi'$$

[52]. Carrying out these transformations of angles, we find that the eigenfunctions (4.19) of \mathbf{J}^2 and J_z behave as

$$\begin{aligned}P\mathcal{Y}_{j l J M}(\theta, \phi; \Theta, \Phi) &= \mathcal{Y}_{j l J M}(\pi - \theta, \pi + \phi; \pi - \Theta, \pi + \Phi) \\ &= (-1)^{j+l} \mathcal{Y}_{j l J M}(\theta, \phi; \Theta, \Phi)\end{aligned}\quad (4.30)$$

where use has been made of the properties of the spherical harmonics (4.10). Thus, $\mathcal{Y}_{j l J M}$ is an eigenfunction not only of \mathbf{J}^2 and J_z , with eigenvalues $J(J+1)$ and M , respectively, but also of the inversion operator, P , with eigenvalue $(-1)^{j+l}$. This latter eigenvalue is denoted by the parity, $p = \pm 1$, of the wave function.

Regarding the eigenfunctions (4.27) of \mathbf{J}^2 and J_Z , the situation is somewhat more complicated. In this case, we find that

$$\begin{aligned}P\mathcal{Z}_{j \Omega J M}(\theta', \phi'; \Theta, \Phi) &= \mathcal{Z}_{j \Omega J M}(\theta', \pi - \phi'; \pi - \Theta, \pi + \Phi) \\ &= (-1)^J \mathcal{Z}_{j, -\Omega J M}(\theta', \phi'; \Theta, \Phi)\end{aligned}\quad (4.31)$$

As Ω appears on the left-hand side, and $-\Omega$ on the right-hand side, of equation (4.31), it follows that, while $\mathcal{Z}_{j \Omega J M}$ is an eigenfunction of \mathbf{J}^2 and J_Z , with eigenvalues $J(J+1)$ and Ω , respectively, it is not an eigenfunction of P . However, such eigenfunctions may readily be formed as the linear combinations

$$\mathcal{Z}_{j \tilde{\Omega} \epsilon J M} = \frac{\left(\mathcal{Z}_{j \tilde{\Omega} J M} + \epsilon \mathcal{Z}_{j, -\tilde{\Omega} J M} \right)}{\left[2(1 + \delta_{\tilde{\Omega} 0}) \right]^{\frac{1}{2}}}\quad (4.32)$$

where $\bar{\Omega} = |\Omega|$ and $\epsilon = \pm 1$. The factor $\left[2(1 + \delta_{\bar{\Omega}0})\right]^{\frac{1}{2}}$ ensures that the eigenfunctions are correctly normalized for all possible values of $\bar{\Omega}$, i.e. for $\bar{\Omega} \geq 0$. It may be seen from equation (4.32) that, when $\Omega = 0$, only $\epsilon = +1$ is allowed: the eigenfunction vanishes when $\epsilon = -1$. The functions $\mathcal{Z}_{j\bar{\Omega}\epsilon JM}$ are eigenfunctions of the inversion operator, P , with eigenvalue $p' = (-1)^J \epsilon$. When $\epsilon = (-1)^{j+l+J}$, that is, when $p' = p$, \mathcal{Y}_{jIJM} and $\mathcal{Z}_{j\bar{\Omega}\epsilon JM}$ are related through

$$\begin{aligned} \mathcal{Y}_{jIJM}(\theta, \phi; \Theta, \Phi) &= \sum_{\bar{\Omega}} \left[\frac{2(2l+1)}{(1 + \delta_{\bar{\Omega}0})(2J+1)} \right]^{\frac{1}{2}} C_{\bar{\Omega}0\bar{\Omega}}^{jIJ} \\ &\times \mathcal{Z}_{j\bar{\Omega}\epsilon JM}(\theta', \phi'; \Theta, \Phi) \end{aligned} \quad (4.33)$$

In matrix notation, equation (4.33) becomes

$$|jIJM\rangle = |j\bar{\Omega}\epsilon JM\rangle \langle j\bar{\Omega}\epsilon JM | jIJM \rangle \quad (4.34)$$

with $\epsilon = (-1)^{j+l+J}$ and an implied summation over $\bar{\Omega} \geq 0$. It follows from the properties of the Clebsch–Gordan coefficients [51] that, when $\bar{\Omega} = 0$, $C_{\bar{\Omega}0\bar{\Omega}}^{jIJ} = C_{000}^{jIJ} = 0$ unless $j + l + J$ is even; this implies that only $\epsilon = (-1)^{j+l+J} = +1$ is allowed when $\bar{\Omega} = 0$, a condition already noted above.

A rotation of the coordinate system, from the SF to the BF frame, leaves the parity of the wave function unchanged. As a consequence, equation (4.33) [or equivalently (4.34)] is applicable only when $p' = p$. With $p' = p = (-1)^J \epsilon$, equation (4.32) may be written in the form

$$\mathcal{Z}_{j\bar{\Omega}pJM} = \frac{\left(\mathcal{Z}_{j\bar{\Omega}JM} + (-1)^J p \mathcal{Z}_{j, -\bar{\Omega}JM} \right)}{\left[2(1 + \delta_{\bar{\Omega}0}) \right]^{\frac{1}{2}}}$$

Similarly, as $p = (-1)^{j+l}$, we may define

$$\mathcal{Y}_{jIpJM} \equiv \mathcal{Y}_{jIJM}$$

where the parity subscript is written explicitly. Either the SF functions $\mathcal{Y}_{jIpJM}(\theta, \phi; \Theta, \Phi)$ or the BF functions $\mathcal{Z}_{j\bar{\Omega}pJM}(\theta', \phi'; \Theta, \Phi)$ are suitable as a basis in which to expand the total wave function, Ψ ,

$$\Psi(\hat{\mathbf{r}}, \mathbf{R}) = \sum_{jIpJM} \frac{F(jIpJM|R)}{R} \mathcal{Y}_{jIpJM}(\hat{\mathbf{r}}; \hat{\mathbf{R}}) \quad (4.35)$$

or

$$\Psi(\hat{\mathbf{r}}', \mathbf{R}) = \sum_{j\bar{\Omega}pJM} \frac{G(j\bar{\Omega}pJM|R)}{R} \mathcal{Z}_{j\bar{\Omega}pJM}(\hat{\mathbf{r}}'; \hat{\mathbf{R}}) \quad (4.36)$$

where $\hat{\mathbf{r}} = (\theta, \phi)$, $\hat{\mathbf{r}}' = (\theta', \phi')$, $\hat{\mathbf{R}} = (\Theta, \Phi)$ and $\mathbf{R} = (R, \Theta, \Phi)$ denote polar coordinates.

The Schrödinger equation (4.5) may be written

$$(H - E)\Psi = 0 \quad (4.37)$$

where the hamiltonian is given by

$$H = \frac{\mathbf{j}^2}{2I} - \frac{\nabla_R^2}{2\mu} + V(R, \theta') \quad (4.38)$$

The first term on the right-hand side of equation (4.38) will be recognized as the rotational energy of a rigid rotor. We recall that the rotational angular momentum of a rotor is $j = I\omega$, where I is the moment of inertia and ω is the angular velocity. The associated kinetic energy is $T = I\omega^2/2 = \mathbf{j}^2/(2I)$. The term $V(R, \theta')$ denotes the potential of interaction between A and BC on a given potential energy surface and was written above [cf. equation (4.9)] as $E_j(\mathbf{R})$. The energy of interaction between an atom A and a rigid rotor BC depends on the BF coordinates R and θ' only; V is independent of ϕ' as the potential is invariant under rotations of the internuclear axis BC about the BF Z -axis. For the purposes of the subsequent analysis, $V(R, \theta')$ is expanded over a complete set of functions of the angular variable, θ' ,

$$V(R, \theta') = \sum_{\lambda=0}^{\infty} v_{\lambda}(R) P_{\lambda}(\cos \theta') \quad (4.39)$$

where P_{λ} is the Legendre polynomial [47]. In practice, the summation in (4.39) is truncated at a finite and sometimes small value of λ .

The second term on the right-hand side of equation (4.38) represents the kinetic energy of the relative motion of A and BC and may be separated into radial and angular parts:

$$-\frac{1}{2\mu} \nabla_R^2 = -\frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\mathbf{l}^2}{2\mu R^2} \quad (4.40)$$

We recall that $\mu = m_A(m_B + m_C)/(m_A + m_B + m_C)$ is the reduced mass of the system A + BC. Thus, equation (4.37) becomes

$$\left[\frac{\mathbf{j}^2}{2I} - \frac{1}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{\mathbf{l}^2}{2\mu R^2} + V(R, \theta') - E \right] \Psi = 0 \quad (4.41)$$

with Ψ given by equation (4.35) or equation (4.36). Recalling that

$$\mathbf{j}^2 \mathcal{Y}_{jlpJM} = j(j+1) \mathcal{Y}_{jlpJM}$$

and

$$\mathbf{j}^2 \mathcal{Z}_{j\bar{\Omega}pJM} = j(j+1) \mathcal{Z}_{j\bar{\Omega}pJM}$$

equation (4.41) may be written

$$\left[-\frac{1}{R} \frac{\partial^2}{\partial R^2} R + \frac{\mathbf{l}^2}{R^2} + 2\mu V(R, \theta') - k_j^2 \right] \Psi = 0 \quad (4.42)$$

where

$$k_j^2 = 2\mu[E - Bj(j+1)] \quad (4.43)$$

and $B = 1/(2I)$ is the rotational constant of the molecule BC.

We may now make use of the orthonormality properties of the basis functions, \mathcal{Y}_{jlpJM} and $\mathcal{Z}_{j\bar{\Omega}pJM}$:

$$\int \mathcal{Y}_{jlpJM}^*(\hat{\mathbf{r}}; \hat{\mathbf{R}}) \mathcal{Y}_{j'l'p'J'M'}(\hat{\mathbf{r}}; \hat{\mathbf{R}}) d\hat{\mathbf{r}} d\hat{\mathbf{R}} = \delta_{jj'} \delta_{ll'} \delta_{pp'} \delta_{JJ'} \delta_{MM'}$$

and

$$\int \mathcal{Z}_{j\bar{\Omega}pJM}^*(\hat{\mathbf{r}}'; \hat{\mathbf{R}}) \mathcal{Z}_{j'\bar{\Omega}'p'J'M'}(\hat{\mathbf{r}}'; \hat{\mathbf{R}}) d\hat{\mathbf{r}}' d\hat{\mathbf{R}} = \delta_{jj'} \delta_{\bar{\Omega}\bar{\Omega}'} \delta_{pp'} \delta_{JJ'} \delta_{MM'}$$

We operate on equation (4.42) from the left with

$$\int d\hat{\mathbf{r}} d\hat{\mathbf{R}} \mathcal{Y}_{jlpJM}^*(\hat{\mathbf{r}}; \hat{\mathbf{R}})$$

or

$$\int d\hat{\mathbf{r}}' d\hat{\mathbf{R}} \mathcal{Z}_{j\bar{\Omega}pJM}^*(\hat{\mathbf{r}}'; \hat{\mathbf{R}})$$

according to whether the SF or the BF expansion, equation (4.35) or (4.36), is used for the wave function, Ψ . Equation (4.42) then reduces to

$$\begin{aligned} & \left[\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} + k_j^2 \right] F(jlpJM|R) \\ &= 2\mu \sum_{j'l'p'J'M'} \langle jlpJM | V(R, \theta') | j'l'p'J'M' \rangle F(j'l'p'J'M'|R) \end{aligned} \quad (4.44)$$

or

$$\begin{aligned} & \left[\frac{d^2}{dR^2} + k_j^2 \right] G(j\bar{\Omega}pJM|R) \\ &= 2\mu \sum_{j'\bar{\Omega}'p'J'M'} \langle j\bar{\Omega}pJM | V(R, \theta') | j'\bar{\Omega}'p'J'M' \rangle \\ & \quad + \frac{l^2}{2\mu R^2} \langle j'\bar{\Omega}'p'J'M' \rangle G(j'\bar{\Omega}'p'J'M'|R) \end{aligned} \quad (4.45)$$

depending on whether the SF or the BF basis functions are used. When deriving equation (4.44), we have made use of the fact that

$$l^2 \mathcal{Y}_{jlpJM} = l(l+1) \mathcal{Y}_{jlpJM}$$

which gives rise to the centrifugal term, $l(l+1)/R^2$. We use the more compact bra-ket notation on the right-hand sides of equations (4.44) and (4.45).

Equations (4.44) and (4.45) are equivalent, and identical cross-sections should be obtained when these equations are solved without further approximation. Both (4.44) and (4.45) represent sets of ordinary differential equations, which are linear in the functions of the radial coordinate, $F(R)$ or $G(R)$, involve second-order derivatives with respect to R , and are 'coupled' through the matrix elements on the right-hand sides. Powerful numerical techniques have been developed for solving such systems of equations and incorporated in the MOLSCAT [53], HIBRIDON [54] and MOLCOL [55] computer codes.

The use of either equation (4.44) or equation (4.45) has its advantages and drawbacks. In (4.44), the centrifugal term takes a simple form because the SF basis functions are eigenfunctions of the operator \mathbf{I}^2 . However, in the matrix elements on the right-hand side, the basis functions depend on the SF coordinate, θ , whereas the potential V depends on the BF coordinate, θ' . The evaluation of these matrix elements will be considered below. In (4.45), on the other hand, the matrix elements involving V may be evaluated directly, as the basis functions also depend on BF coordinates. In this case, it is the operator representing the centrifugal potential, $\mathbf{I}^2/(2\mu R^2)$ that poses problems: because the BF coordinate system is itself rotating, not only centrifugal but also Coriolis terms arise when evaluating this operator, the expression for which will be given below.

4.3.1 *The space-fixed (SF) basis functions*

We consider the matrix elements of the potential,

$$\begin{aligned} \langle jlpJM | V(R, \theta') | j'l'p'J'M' \rangle \\ = \int \mathcal{Y}_{jlpJM}^*(\hat{\mathbf{r}}; \hat{\mathbf{R}}) V(R, \theta') \mathcal{Y}_{j'l'p'J'M'}(\hat{\mathbf{r}}; \hat{\mathbf{R}}) d\hat{\mathbf{r}} d\hat{\mathbf{R}} \\ = \sum_{\lambda} \nu_{\lambda}(R) \int \mathcal{Y}_{jlpJM}^*(\hat{\mathbf{r}}; \hat{\mathbf{R}}) P_{\lambda}(\cos \theta') \mathcal{Y}_{j'l'p'J'M'}(\hat{\mathbf{r}}; \hat{\mathbf{R}}) d\hat{\mathbf{r}} d\hat{\mathbf{R}} \end{aligned} \quad (4.46)$$

where we introduce the expansion (4.39) of the potential V in terms of the Legendre polynomials, P_{λ} . The integral (4.46) may be evaluated by means of the spherical harmonic addition theorem [48], which states that

$$P_{\lambda}(\cos \theta') = \frac{4\pi}{2\lambda + 1} \sum_{\nu=-\lambda}^{\lambda} Y_{\lambda\nu}(\hat{\mathbf{r}}) Y_{\lambda\nu}^*(\hat{\mathbf{R}}) \quad (4.47)$$

where $Y_{\lambda\nu}$ is a spherical harmonic function, given by (4.10) above. This theorem converts the dependence of the potential on θ' , which is the angle between the intramolecular vector $\hat{\mathbf{r}}$ and the intermolecular vector $\hat{\mathbf{R}}$ (see Fig. 4.2), into its dependence on the SF angles $\hat{\mathbf{r}} = (\theta, \phi)$ and $\hat{\mathbf{R}} = (\Theta, \Phi)$ and enables the integrals in equation (4.46) to be carried out. Using the definition (4.19) of the SF basis functions and the composition relations for spherical harmonics [48],

$$\int Y_{jm}^*(\hat{\mathbf{r}}) Y_{\lambda\nu}(\hat{\mathbf{r}}) Y_{j'm'}(\hat{\mathbf{r}}) d\hat{\mathbf{r}} = \left[\frac{(2j' + 1)(2\lambda + 1)}{4\pi(2j + 1)} \right]^{\frac{1}{2}} C_{m'\nu m}^{j'\lambda j} C_{000}^{j'\lambda j} \quad (4.48)$$

and

$$\int Y_{lm_l}^*(\hat{\mathbf{R}}) Y_{\lambda\nu}^*(\hat{\mathbf{R}}) Y_{l'm_{l'}}(\hat{\mathbf{R}}) d\hat{\mathbf{R}} = \left[\frac{(2l+1)(2\lambda+1)}{4\pi(2l'+1)} \right]^{\frac{1}{2}} C_{m_l\nu m_{l'}}^{l\lambda l'} C_{000}^{l\lambda l'} \quad (4.49)$$

Equation (4.46) becomes

$$\begin{aligned} \langle jlpJM | V(R, \theta') | j'l'p'J'M' \rangle \\ = \sum_{\lambda\nu} \nu_{\lambda}(R) \left[\frac{(2j'+1)(2l+1)}{(2j+1)(2l'+1)} \right]^{\frac{1}{2}} C_{000}^{j'\lambda j} C_{000}^{l\lambda l'} \\ \times \sum_{mm_l m' m_{l'}} C_{mm_l M}^{jIJ} C_{m'\nu m}^{j'\lambda j} C_{m' m_{l'} M'}^{j' l' J'} C_{m_l \nu m_{l'}}^{l\lambda l'} \end{aligned} \quad (4.50)$$

Using angular momentum recoupling theory (see, for example, [51]), equation (4.50) may be expressed in terms of a Racah coefficient, W :

$$\begin{aligned} \langle jlpJM | V(R, \theta') | j'l'p'J'M' \rangle \\ = \delta_{JJ'} \delta_{MM'} (-1)^{j+j'-J} \sum_{\lambda} \nu_{\lambda}(R) \frac{[(2j+1)(2l+1)(2j'+1)(2l'+1)]^{\frac{1}{2}}}{(2\lambda+1)} \\ \times C_{000}^{jj'\lambda} C_{000}^{ll'\lambda} W(jlj'l'; J\lambda) \end{aligned} \quad (4.51)$$

The Racah coefficient is related to the $6j$ -symbol of Wigner through

$$W(jlj'l'; J\lambda) = (-1)^{j+l+j'+l'} \left\{ \begin{matrix} j & l & J \\ l' & j' & \lambda \end{matrix} \right\} \quad (4.52)$$

and is an algebraic quantity that is readily evaluated for given values of the arguments. The Kronecker δ symbols appearing in (4.51) ensure the conservation of the total angular momentum, J , and its projection M , on the SF z -axis. As $C_{000}^{jj'\lambda}$ and $C_{000}^{ll'\lambda}$ vanish identically unless $j+j'+\lambda$ and $l+l'+\lambda$, respectively, are even, we see that

$$(-1)^{j+j'+\lambda+l+l'+\lambda} = +1 = (-1)^{j+l+j'+l'} \quad (4.53)$$

because λ is an integer. It follows that

$$p = (-1)^{j+l} = (-1)^{j'+l'} = p' \quad (4.54)$$

i.e. the parity is conserved. Using these conservation relations, we may write equation (4.51) in the more compact form

$$\langle jlpJM | V(R, \theta') | j'l'pJM \rangle = \sum_{\lambda} \nu_{\lambda}(R) f_{\lambda}(jl, j'l'; J) \quad (4.55)$$

where the algebraic coefficient

$$f_{\lambda}(jl, j'l'; J) = (-1)^{j+j'-J} \frac{[(2j+1)(2l+1)(2j'+1)(2l'+1)]^{\frac{1}{2}}}{(2\lambda+1)} \\ \times C_{000}^{jj'\lambda} C_{000}^{ll'\lambda} W(jl j'l'; J\lambda) \quad (4.56)$$

is independent of the projection quantum number M . The coefficients $f_{\lambda}(jl, j'l'; J)$ were first introduced by Percival and Seaton [46], who were concerned with e^- -H scattering (see Chapter 9), and are often referred to as 'Percival-Seaton coefficients'. The coupled equations (4.44) may now be written

$$\left[\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} + k_j^2 \right] F(jl p J | R) \\ = 2\mu \sum_{j'l'\lambda} v_{\lambda}(R) f_{\lambda}(jl, j'l'; J) F(j'l' p J | R) \quad (4.57)$$

where the index M has been dropped, as the equations are independent of this quantum number.

It is instructive to consider the form of these equations for $\lambda = 0$. In this case, the Clebsch-Gordan coefficients in (4.56) are non-vanishing only when $j = j'$ and $l = l'$, and hence no collisional coupling between different rotational states of the molecule BC can occur. The term with $\lambda = 0$ in the interaction potential (4.39) is *angle independent*, as $P_0(\cos \theta') = 1$, and cannot induce rotational excitation (or de-excitation) of the molecule; $v_0(R)$ contributes only to *elastic scattering* of A on BC. Terms in the potential with $\lambda \geq 1$, on the other hand, can give rise to rotational transitions in the molecule, subject to the *triangular inequalities* $|j - j'| \leq \lambda \leq j + j'$ and the requirement that $j + j' + \lambda$ should be an even integer. Thus, if $j = 0$, $\lambda = j' = j' - j \equiv \Delta j$. In the CO molecule, for example, excitation from the ground state, $j = 0$, to $j' = 1$ is induced by the term with $\lambda = 1$ in the interaction potential. Similarly, direct excitation from $j = 0$ to $j' = 2$ is induced by the following term, with $\lambda = 2$, and so on. The absolute magnitudes of successive coefficients $v_{\lambda}(R)$ in the expansion of the potential (4.39) tend to decrease as λ increases, and the probability of transitions involving increasing values of Δj becomes progressively smaller.

In the case of *homonuclear* molecules, where B and C are identical (H_2 , N_2 , O_2 , ...), the interaction potential is clearly invariant under exchange of B and C, equivalent to the operation $\theta' \rightarrow \pi - \theta'$. As $\cos(\pi - \theta') = -\cos \theta'$, and

$$P_{\lambda}(-\cos \theta') = P_{\lambda}(\cos \theta')$$

when λ is even, and

$$P_{\lambda}(-\cos \theta') = -P_{\lambda}(\cos \theta')$$

when λ is odd, it follows that only those terms with even values of λ appear in the interaction potential. As $j + j' + \lambda$ must also be an even integer, collisional transitions between even and odd values of the rotational quantum number j cannot occur.

4.3.2 The body-fixed (BF) basis functions

We must evaluate the matrix elements of the *effective potential*, $V_{\text{eff}}(r, \theta')$, comprising the interaction potential, $V(R, \theta')$, and the centrifugal potential, $\mathbf{l}^2/(2\mu R^2)$:

$$\begin{aligned} & \langle j\bar{\Omega}pJM | V(R, \theta') + \frac{\mathbf{l}^2}{(2\mu R^2)} | j'\bar{\Omega}'p'J'M' \rangle \\ &= \int \mathcal{Z}_{j\bar{\Omega}pJM}^*(\hat{\mathbf{r}}'; \hat{\mathbf{R}}) \left[V(R, \theta') + \frac{\mathbf{l}^2}{(2\mu R^2)} \right] \mathcal{Z}_{j'\bar{\Omega}'p'J'M'}(\hat{\mathbf{r}}'; \hat{\mathbf{R}}) d\hat{\mathbf{r}}' d\hat{\mathbf{R}} \end{aligned} \quad (4.58)$$

The contribution of the interaction potential to this integral is readily evaluated. Using the definition of the BF basis functions (4.27), the relation

$$P_\lambda(\cos \theta') = \left(\frac{4\pi}{2\lambda + 1} \right)^{\frac{1}{2}} Y_{\lambda 0}(\theta', \phi') \quad (4.59)$$

the orthogonality relation for the rotation matrix elements

$$\int D_{M\Omega}^J(\Phi, \Theta, 0) D_{M'\Omega'}^{J'}(\Phi, \Theta, 0) \sin \Theta d\Theta d\Phi = \delta_{JJ'} \delta_{MM'} \left(\frac{4\pi}{2J + 1} \right) \quad (4.60)$$

and the composition relation for spherical harmonics

$$\int Y_{j\Omega}^*(\hat{\mathbf{r}}') Y_{\lambda 0}(\hat{\mathbf{r}}') Y_{j'\Omega'}(\hat{\mathbf{r}}') d\hat{\mathbf{r}}' = \delta_{\Omega\Omega'} \left[\frac{(2j' + 1)(2\lambda + 1)}{4\pi(2j + 1)} \right]^{\frac{1}{2}} C_{\Omega 0 \Omega}^{j' \lambda j} C_{000}^{j' \lambda j} \quad (4.61)$$

we obtain

$$\begin{aligned} & \langle j\bar{\Omega}pJM | V(R, \theta') | j'\bar{\Omega}'p'J'M' \rangle \\ &= \delta_{\bar{\Omega}\bar{\Omega}'} \delta_{pp'} \delta_{JJ'} \delta_{MM'} (-1)^{\bar{\Omega}} \sum_{\lambda} \nu_{\lambda}(R) \frac{[(2j + 1)(2j' + 1)]^{\frac{1}{2}}}{(2\lambda + 1)} \\ & \quad \times C_{000}^{jj' \lambda} C_{\bar{\Omega}, -\bar{\Omega} 0}^{jj' \lambda} \end{aligned} \quad (4.62)$$

Equation (4.62) incorporates the same conservation properties ($J = J'$, $M = M'$, $p = p'$) as those encountered above in the discussion of the matrix elements of the potential in the SF representation. In addition, we have the relation $\bar{\Omega} = \bar{\Omega}'$. This latter property arises from the invariance of the potential under rotations about the BF Z-axis, that is, from the fact that V is independent of ϕ' . The torque about the Z-axis is $\Gamma_Z = -\partial V / \partial \phi'$, and it follows that the component of the angular momentum, Ω , about this same axis cannot be modified by the interaction potential. On the other hand, the angular momentum operator, \mathbf{l}^2 , *can* change the value of Ω . Using the quantum theory of angular momentum, it may be shown that the non-vanishing matrix elements of the centrifugal potential operator in equation (4.58)

are given by

$$\begin{aligned} \langle j\bar{\Omega}pJM | \frac{\mathbf{I}^2}{2\mu R^2} | j\bar{\Omega}pJM \rangle \\ = \frac{J(J+1) + j(j+1) - 2\bar{\Omega}^2}{2\mu R^2} \end{aligned} \quad (4.63)$$

and

$$\begin{aligned} \langle j\bar{\Omega}pJM | \frac{\mathbf{I}^2}{2\mu R^2} | j, \bar{\Omega} \pm 1, pJM \rangle \\ = -(1 + \delta_{\bar{\Omega}0})^{\frac{1}{2}} (1 + \delta_{\bar{\Omega} \pm 1, 0})^{\frac{1}{2}} \\ \times \frac{[J(J+1) - \bar{\Omega}(\bar{\Omega} \pm 1)]^{\frac{1}{2}} [j(j+1) - \bar{\Omega}(\bar{\Omega} \pm 1)]^{\frac{1}{2}}}{2\mu R^2} \end{aligned} \quad (4.64)$$

[45, 52, 56]. These results are to be compared with $l(l+1)/(2\mu R^2)$, the corresponding matrix elements when SF functions are used. The reason for the additional complexity of equations (4.63) and (4.64) – Coriolis forces in the BF frame – has already been mentioned.

Inspection of equations (4.62–4.64) shows the matrix elements of both the interaction potential and the centrifugal potential to be independent of the projection quantum number, M . Accordingly, the coupled equations (4.45) may be written

$$\begin{aligned} \left[\frac{d^2}{dR^2} + k_j^2 \right] G(j\bar{\Omega}pJ|R) \\ = 2\mu \sum_{j'\bar{\Omega}'} V_{\text{eff}}(j\bar{\Omega}, j'\bar{\Omega}'; J|R) G(j'\bar{\Omega}'pJ|R) \end{aligned} \quad (4.65)$$

where $V_{\text{eff}}(j\bar{\Omega}, j'\bar{\Omega}'; J|R)$ denotes a matrix element (4.58) of the effective potential,

$$V_{\text{eff}}(R, \theta') = V(R, \theta') + \mathbf{I}^2/(2\mu R^2) \quad (4.66)$$

These equations have a form that is clearly similar to the SF-coupled equations (4.57), and they can be solved by means of the same algorithms.

In summary, Schrödinger's equation for the collision between an atom A and a diatomic molecule BC may be reduced to a set of coupled differential equations. These equations have a similar structure when written in terms of SF or BF coordinates; the Z-axis of the BF coordinate system is chosen to coincide with the vector from the centre of mass M of the molecule to the atom A. The matrix elements of the interaction potential are more tricky to evaluate in the SF frame than in the BF frame, whereas, for the matrix elements of the centrifugal potential, the opposite is true.

One reason for deriving both forms, (4.57) and (4.65), of the coupled equations is that they lend themselves to different types of approximation. The centrifugal potential, $\mathbf{I}^2/(2\mu R^2)$, varies as R^{-2} , whereas, in the collision between a neutral atom and a neutral molecule, the leading term in the potential energy expansion (4.39) varies as R^{-6} at long range.

This comparison suggests that collisions at long range, that is, collisions at large values of the impact parameter and hence of the relative angular momentum, l , might be solved by means of the SF equations with an approximate form of the interaction potential. A possible approximation consists of truncating the potential energy expansion to just a few terms. On the other hand, short-range collisions and small values of l could be solved by means of the BF equations and an approximate form of the centrifugal potential.

Rotationally inelastic collisions involving neutral particles tend to be induced by the interaction potential at short range and lend themselves to approximations based upon the BF-coupled equations; the related approximations will now be presented. Rotationally inelastic collisions form an important category of astrophysical processes. Approximate methods are, and are likely to continue to be, essential aids to solving certain types of molecular collision problems; they are helpful also in understanding the physics involved in such processes.

4.3.3 The coupled states (CS) approximation

The coupled states, or centrifugal decoupling, approximation was introduced by McGuire and Kouri [57]; it has proved to be one of the most successful approximations and has been used extensively in studies of rotational and also vibrational excitation processes. McGuire and Kouri used the BF formulation of the scattering of an atom on a rigid rotor, with the matrix elements of the centrifugal potential, (4.63) and (4.64), approximated by their SF equivalent forms, that is,

$$(j\bar{\Omega}pJM|l^2/(2\mu R^2)|j\bar{\Omega}'pJM) \approx \delta_{\bar{\Omega}\bar{\Omega}'} l(l+1)/(2\mu R^2) \quad (4.67)$$

We see from (4.67) that, subject to this approximation, the centrifugal potential conserves the value of the projection quantum number, $\bar{\Omega}$. As the interaction potential also conserves $\bar{\Omega}$ [cf. equation (4.62)], McGuire and Kouri called this approximation the ' j_z -conserving coupled states approximation'. The BF equations (4.65) are now coupled only through the rotational quantum number, j . Thus, the problem reduces to solving, for each value of $\bar{\Omega}$, a set of differential equations coupled in j , rather than a single set of equations, coupled in both j and $\bar{\Omega}$.

The consequent saving in computing time can be substantial, sometimes rendering feasible calculations which would not be practical otherwise. We recall that, as Ω is the projection of both \mathbf{j} and \mathbf{J} on the BF Z-axis, and $\bar{\Omega} = |\Omega|$, the quantum theory of angular momentum requires that

$$\begin{aligned} \bar{\Omega} &= 0, 1, \dots, \min(j, J) \quad [p = (-1)^J] \\ \bar{\Omega} &= 1, 2, \dots, \min(j, J) \quad [p = -(-1)^J] \end{aligned}$$

where $\min(j, J)$ denotes the lesser of j and J . For a problem involving the rotational states $j = 0, 1, \dots, j_{\max}$ and for $J > j_{\max}$, the corresponding numbers of coupled equations are

$$\begin{aligned} N &= \sum_{j=0}^{j_{\max}} (j+1) = (j_{\max}+1)(j_{\max}+2)/2 \quad [p = (-1)^J] \\ N &= \sum_{j=0}^{j_{\max}} j = j_{\max}(j_{\max}+1)/2 \quad [p = -(-1)^J] \end{aligned}$$

Depending on the algorithm that is used, the computer time requirement, T , can increase with N as rapidly as $T \propto N^3$. The numerical solution of the complete sets of coupled equations then requires a time $T \propto j_{\max}^6/4$ for large j_{\max} . On the other hand, when the CS approximation is employed, the number of coupled channels is $(j_{\max} + 1)$ for $\bar{\Omega} = 0$, j_{\max} for $\bar{\Omega} = 1$, $(j_{\max} - 1)$ for $\bar{\Omega} = 2$, and so on, up to 1 channel for $\bar{\Omega} = j_{\max}$. The corresponding computer time requirement is

$$T \propto \sum_{j=0}^{j_{\max}} [(j+1)^3 + j^3] \sim j_{\max}^4/2$$

Thus, the CS approximation is more rapid by a factor $\sim j_{\max}^2/2$. Even when modest numbers of rotational levels are involved, $j_{\max} \approx 5$, say, using the CS approximation can be about an order of magnitude faster than solving the complete sets of coupled equations.

4.3.4 *The infinite order sudden (IOS) approximation*

As was recognized by McGuire and Kouri [57], the essence of the CS approximation is to neglect the rotation in space of the BF coordinate system when evaluating the centrifugal potential. If the *sudden* approximation to the rotation of the diatomic molecule is also applicable, that is, if the molecule does not rotate appreciably in the course of the collision, then $\theta' \approx \text{constant}$. This additional approximation is most appropriate for heavy molecules that rotate only slowly and have small rotational constants, B , at collision energies, E , that are large compared with the rotational excitation energies, $Bj(j+1)$, of the levels in question. Then, it follows from (4.43) that

$$k_j^2 = 2\mu[E - Bj(j+1)] \approx 2\mu E \equiv k^2 \quad (4.68)$$

and the scattering equations (4.42) reduce to

$$\left[\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} - 2\mu V(R, \theta') + k^2 \right] G_l(R, \theta') = 0 \quad (4.69)$$

which is to be solved for given values of the parameters θ' and l .

The combination of the centrifugal decoupling and the energy sudden approximations, which leads to equations of the relatively simple form (4.69), is known as the infinite order sudden (IOS) approximation; it derives from the work of Tsien and Pack [58–60] and Pack [61]. This approximation was used extensively in studies of rotational and rovibrational excitation, in a form due to Secrest [62]. The problem of rovibrational excitation will be considered in Chapter 5. The use of the IOS approximation is sometimes necessary, but the CS approximation is certainly to be preferred, whenever its use is feasible.

4.3.5 *Boundary conditions*

The differential equations derived above, whether exact or approximate, are to be solved subject to appropriate boundary conditions. In order to illustrate the principles involved, we shall consider the form of the boundary conditions which are appropriate when the simplest approximation to the coupled equations, the IOS approximation, is employed.

We are concerned with problems such that

$$V(R, \theta') \gg E$$

as $R \rightarrow 0$, and

$$V(R, \theta') \sim R^{-n}$$

as $R \rightarrow \infty$, where $n \geq 2$ is an integer. The scattering boundary conditions appropriate to this form of potential are

$$G_l(R, \theta') \rightarrow 0$$

as $R \rightarrow 0$, and

$$G_l(R, \theta') \sim k^{\frac{1}{2}} R [j_l(kR)A_l(\theta') - n_l(kR)B_l(\theta')] \quad (4.70)$$

as $R \rightarrow \infty$; j_l and n_l are *spherical Bessel functions* of the first and second kinds, respectively [47]. The coefficients $A_l(\theta')$ and $B_l(\theta')$ are determined by solving numerically the differential equations (4.69), using one of a number of possible algorithms, and fitting to the form (4.70) in the asymptotic region, where the interaction potential has become vanishingly small (in practice, small compared with the collision energy, E).

All relevant information on the scattering process is contained in the quantity

$$S_l(\theta') = 1 + 2iK_l(\theta')[1 - iK_l(\theta')]^{-1} \quad (4.71)$$

where $i = (-1)^{\frac{1}{2}}$ and $K_l(\theta')$ is given by

$$K_l(\theta') = B_l(\theta')A_l^{-1}(\theta') \quad (4.72)$$

Equations (4.70–4.72) are readily generalized to coupled channels scattering, when \mathbf{K} and \mathbf{S} are known as the *reactance* and *scattering* matrices, respectively [63].

Equation (4.71), which derives from the sudden approximation to the scattering process, does not in itself yield information on rotationally *inelastic* scattering, that is, on scattering processes involving a change in the rotational state of the molecule. However, this information may be obtained from

$$\begin{aligned} S_l(j\Omega, j'\Omega') &\equiv \langle j\Omega | S_l(\theta') | j'\Omega' \rangle \\ &= \int_{\theta'=0}^{\pi} \int_{\phi'=0}^{2\pi} Y_{j\Omega}^*(\theta', \phi') S_l(\theta') Y_{j'\Omega'}(\theta', \phi') \sin \theta' d\theta' d\phi' \\ &= \delta_{\Omega\Omega'} 2\pi \int_{\theta'=0}^{\pi} Y_{j\Omega}^*(\theta', 0) S_l(\theta') Y_{j'\Omega}(\theta', 0) \sin \theta' d\theta' \end{aligned} \quad (4.73)$$

Such integrals can be evaluated by means of numerical quadrature, having determined $S_l(\theta')$ at the appropriate values of θ' by solving the scattering equation (4.69). Partial cross-sections (i.e. the contributions to the total cross-sections from each value of l) may then be derived from

$$\sigma_l(j \leftarrow j') = \frac{\pi}{k_j^2(2j' + 1)} \sum_{\Omega} (2l + 1) |S_l(j\Omega, j'\Omega)|^2 \quad (j \neq j') \quad (4.74)$$

and total cross-sections by summing over l .

An alternative form of (4.74), which is better adapted to discussion, is

$$\sigma_l(j \leftarrow j') = \frac{\pi}{k_{j'}^2} (2l + 1) P_l(j \leftarrow j') \quad (4.75)$$

where

$$P_l(j \leftarrow j') = \frac{1}{(2j' + 1)} \sum_{\Omega} |S_l(j\Omega, j'\Omega)|^2 \quad (j \neq j') \quad (4.76)$$

is the *probability* of the $j \leftarrow j'$ rotationally inelastic transition. The *total* cross-section is

$$\begin{aligned} \sigma(j \leftarrow j') &= \sum_l \sigma_l(j \leftarrow j') \\ &= \frac{\pi}{k_{j'}^2} \sum_l (2l + 1) P_l(j \leftarrow j') \end{aligned} \quad (4.77)$$

Equation (4.77) is the quantum mechanical equivalent of the semi-classical expression for a cross-section as an integral of the corresponding transition probability over the impact parameter

$$\sigma(j \leftarrow j') = 2\pi \int_0^\infty P_b(j \leftarrow j') b \, db \quad (4.78)$$

The impact parameter, b , is defined as the distance of closest approach of the atom A to the centre of mass M of the molecule BC, if the atom were to follow a straight-line trajectory. The *semi-classical* transition probability, $P_b(j \leftarrow j')$, is a function of the *classical* impact parameter for a given transition between the *quantized* states of the molecule. To derive (4.77) from (4.78), we note the correspondence between the classical and quantal expressions for the square of the relative angular momentum,

$$2\mu E b^2 = l(l + 1) = k^2 b^2$$

where k is the wave number. Differentiating for a given (constant) value of E , we obtain

$$2k^2 b \, db = (2l + 1) \, dl$$

where $dl = 1$ in the quantal limit.

It may be seen from (4.77) or (4.78) that the basic task of either a quantum mechanical or a semi-classical calculation of a collision process is to evaluate the transition probabilities, P_l or P_b , respectively. In subsequent applications of the results, the quantity that is required is the rate coefficient, which is related to the cross-section through

$$\langle \sigma v \rangle_{j \leftarrow j'} = \int_0^\infty v_{j'} \sigma_{j \leftarrow j'}(v_{j'}) f(v_{j'}, T) \, dv_{j'} \quad (4.79)$$

where $v_{j'}$ denotes the relative collision velocity of the atom and molecule in the initial channel, j' , and $f(v, T)$ is the Maxwellian velocity distribution at kinetic temperature, T . A Maxwellian distribution is almost always adopted, on the grounds that the timescale for

elastic collisions with the most abundant species (H, He or H₂), which tend to thermalize the velocity distribution, is less than the timescale for inelastic collisions, which have smaller cross-sections. Furthermore, in the astrophysical context, the actual velocity distribution cannot be determined, in general. From detailed balance, we have that

$$\sigma(j \leftarrow j') k_j^2 \omega_{j'} = \sigma(j' \leftarrow j) k_{j'}^2 \omega_j \quad (4.80)$$

where the wave number, k_j , is given by

$$k_j = \frac{\mu v_j}{\hbar}$$

and where μ is the reduced mass of the atom–molecule system. The statistical weight (degeneracy), ω_j , is

$$\omega_j = 2j + 1$$

Equation (4.79) may be written as

$$\langle \sigma v \rangle_{j \leftarrow j'} = \frac{\hbar^2}{\omega_{j'}} \left(\frac{2\pi}{\mu^3 k_B T} \right)^{\frac{1}{2}} \int_0^\infty \Omega_{jj'}(x_{j'}) e^{-x_{j'}} dx_{j'} \quad (4.81)$$

where $\hbar = h/(2\pi)$ and h is Planck's constant, k_B is Boltzmann's constant, and

$$\pi \Omega_{jj'} = \sigma(j \leftarrow j') k_{j'}^2 \omega_{j'}$$

or, from (4.77),

$$\Omega_{jj'} = (2j' + 1) \sum_l (2l + 1) P_l(j \leftarrow j') \quad (4.82)$$

The dimensionless quantity, $\Omega_{jj'}$, termed the *collision strength* in the theory of electron–atom scattering, is symmetric in j and j' . Substituting numerical values for the constants in (4.81), we obtain, in $\text{cm}^3 \text{s}^{-1}$, the units customarily used for rate coefficients,

$$\langle \sigma v \rangle_{j \leftarrow j'} = \frac{1.11 \times 10^{-10}}{\omega_{j'} T^{\frac{1}{2}}} \int_0^\infty \Omega_{jj'}(x_{j'}) e^{-x_{j'}} dx_{j'} \quad (4.83)$$

In problems involving rotational excitation, the numerical value of the summation in (4.82) is typically of the order of 1, and so the corresponding rate coefficients (4.83) are of the order of $10^{-11} \text{ cm}^3 \text{s}^{-1}$ for $T \approx 100 \text{ K}$.

4.4 The rotational excitation of non-linear molecules

Many important interstellar molecules have non-linear structures. Fortunately, they generally retain some symmetry properties that can be exploited to make numerical calculations more tractable; these same properties also lead to *collisional propensity rules*. Examples of such molecules are ammonia (NH₃), a symmetric top, water (H₂O), an asymmetric top, and methanol (CH₃OH), which is a near-symmetric top that exhibits internal torsional motion of the CH₃ relative to the OH group. Each of these examples of classes of molecules will now be discussed.

4.4.1 Symmetric tops

The structure of symmetric top molecules such as ammonia was considered in the classic text of Townes and Shawlow [64]. In the case of NH_3 , the three hydrogen nuclei form an equilateral triangle, and the nitrogen nucleus is on the line perpendicular to this plane and passing through the geometrical centre of the triangle. The molecule can perform end-over-end rotational motion, which we shall treat using the 'rigid rotor' approximation. We denote the rotational quantum number by j , the projection of the rotational angular momentum on the symmetry axis of the molecule by k , and its projection on the space-fixed z -axis by m . The internal hamiltonian is three-fold symmetric about the symmetry axis of the molecule, i.e. the hamiltonian is invariant under a rotation through 120° about this axis, which is the body-fixed Z -axis.

The three hydrogen nuclei (protons) are identical fermions, which obey Fermi–Dirac statistics. Accordingly, the wave function must be asymmetric under exchange of any pair of protons. Townes and Shawlow [64] showed that this constraint leads to an association of rotational states for which $k = 3n$, where $n = 0, 1, 2, \dots$, with the 'parallel' nuclear spin state, $I = 3/2$ (ortho- NH_3). On the other hand, the rotational states with $k = 3n + 1, 3n + 2$ are associated with the 'anti-parallel' nuclear spin state, $I = 1/2$ (para- NH_3). Although the nuclear spin degeneracy of ortho- NH_3 ($2I + 1 = 4$) is twice that of para- NH_3 ($2I + 1 = 2$), the latter has twice as many rotational states (j, k): in any set of three consecutive values of k , two belong to para but only one to ortho. It follows that the total statistical weights of the ortho and the para levels are equal to 4. [Compare this with the case of H_2 , where the total statistical weights of the ortho and para levels are 3 and 1, respectively.]

The internal rotational hamiltonian of a top may be written as

$$h = \frac{j_X^2}{2I_X} + \frac{j_Y^2}{2I_Y} + \frac{j_Z^2}{2I_Z} \quad (4.84)$$

where j_X, j_Y, j_Z are the components of the rotational angular momentum, \mathbf{j} , along the internal BF axes X, Y, Z ; the Z -axis is taken to be the symmetry axis of the molecule. I_X, I_Y, I_Z are the moments of inertia along the BF axes. When the BF axes are taken to coincide with the principal axes of the molecule, the moment of inertia tensor, \mathbf{I} , is diagonal:

$$\mathbf{I} = \begin{pmatrix} I_X & 0 & 0 \\ 0 & I_Y & 0 \\ 0 & 0 & I_Z \end{pmatrix}$$

In a symmetric top molecule, such as ammonia, $I_X = I_Y$. As $\mathbf{j}^2 = j_X^2 + j_Y^2 + j_Z^2$, the rotational hamiltonian takes the form

$$h = \frac{\mathbf{j}^2}{2I_X} + \left(\frac{1}{2I_Z} - \frac{1}{2I_X} \right) j_Z^2 \quad (4.85)$$

The rotational eigenfunction, $|jkm\rangle$ [see equation (4.87) below], is an eigenfunction of \mathbf{j}^2 with eigenvalue $j(j+1)$, of j_Z with eigenvalue k , and of j_z with eigenvalue m (all in atomic units). Hence, we have the relation

$$h|jkm\rangle = \left[\frac{j(j+1)}{2I_X} + \left(\frac{1}{2I_Z} - \frac{1}{2I_X} \right) k^2 \right] |jkm\rangle \quad (4.86)$$

where the eigenvalues of the rotational hamiltonian are given by the term in square brackets in equation (4.86). To each value of the rotational quantum number, j , there correspond $(2j + 1)$ values of the projection quantum number, $k = -j, -j + 1, \dots, 0, \dots, j - 1, j$. However, the expression for the eigenvalue involves k^2 , and so the states $k = |k|$ and $k = -|k|$ are degenerate, i.e. they have the same eigenenergy.

The eigenfunctions, $|jkm\rangle$, of the rotational hamiltonian, h , are expressible in terms of the elements of the rotation matrix, \mathbf{D} [cf. equation (4.12)], appropriately normalized, namely

$$|jkm\rangle = \left(\frac{2j+1}{8\pi^2}\right)^{-\frac{1}{2}} D_{mk}^{j*}(\alpha, \beta, \gamma) \quad (4.87)$$

where (α, β, γ) are the Euler angles that rotate the SF coordinate system into the BF system, defined above. As states $|jkm\rangle$ and $|j, -km\rangle$ are degenerate, the linear combinations

$$|jkm\epsilon\rangle = [2(1 + \delta_{k0})]^{-\frac{1}{2}} (|jkm\rangle + \epsilon |j, -km\rangle) \quad (4.88)$$

with $\epsilon = \pm 1$ are also eigenfunctions of h with the same eigenenergy. The states with $\epsilon = \pm 1$ may be identified with the components of the *inversion doublets* which occur in NH_3 , for $k > 0$, owing to the inversion motion of the nitrogen nucleus through the plane of the hydrogens. The state for which $(-1)^j \epsilon = +1$ is the asymmetric (upper) inversion state, whereas the state for which $(-1)^j \epsilon = -1$ is the symmetric (lower) inversion state. It may be seen from equation (4.88) that only the states with $\epsilon = +1$ exist when $k = 0$; this implies that the lower (symmetric) inversion state is missing when $k = 0$ and j is even, and the upper (asymmetric) inversion state is missing when $k = 0$ and j is odd.

In practice, the inversion motion raises the degeneracy (i.e. gives rise to a splitting) of the states with $\epsilon = +1$ and $\epsilon = -1$. This splitting is small compared with the separation of the rotational levels and is neglected in the rigid rotor approximation. Nonetheless, this splitting is important spectroscopically: transitions between the two components of an inversion doublet ('inversion transitions') enable interstellar ammonia to be observed from the ground, at radio wavelengths.

The rotational excitation of NH_3 by He was studied by Green [65, 66]. We shall follow his approach, treating the molecule as a rigid symmetric top. In Fig. 4.3 the coordinates describing the interaction between NH_3 and He are shown schematically. The BF axes (X, Y, Z) provide a reference frame in which to locate the He atom, whose spherical polar coordinates are (R, θ', ϕ') . The interaction potential may be expanded in the form

$$\begin{aligned} V(R, \theta', \phi') &= \sum_{\lambda} \sum_{\mu=-\lambda}^{\lambda} v_{\lambda\mu}(R) Y_{\lambda\mu}(\theta', \phi') \\ &= \sum_{\lambda} \sum_{\mu=0}^{\lambda} v_{\lambda\mu}(R) \frac{Y_{\lambda\mu}(\theta', \phi') + (-1)^{\mu} Y_{\lambda,-\mu}(\theta', \phi')}{1 + \delta_{\mu 0}} \end{aligned} \quad (4.89)$$

When writing (4.89), use is made of the facts that V is real and symmetric with respect to reflection in the XZ plane, and of the property

$$Y_{\lambda\mu}^*(\theta', \phi') = (-1)^{\mu} Y_{\lambda,-\mu}(\theta', \phi')$$

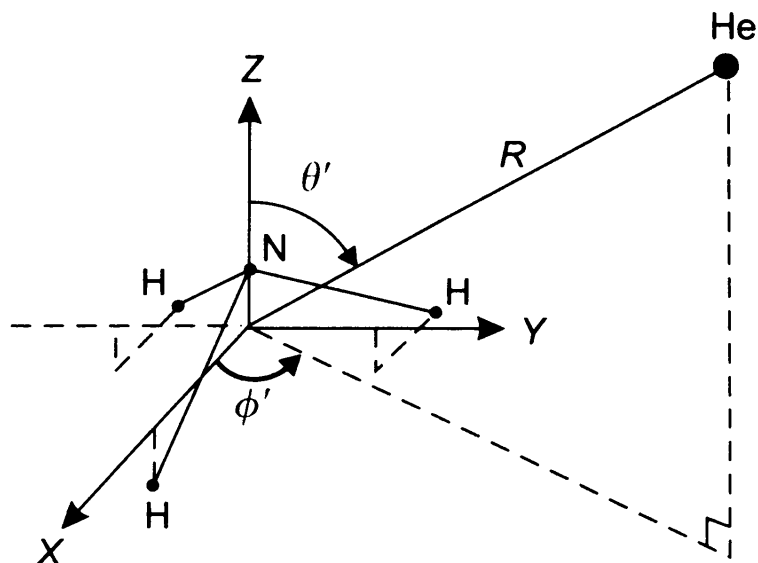


Figure 4.3 Defining the body-fixed coordinate system XYZ of NH_3 , a symmetric top; the origin of the coordinate system is at the centre of mass of the molecule. The spherical polar coordinates (R, θ', ϕ') , determine the position of the He atom, relative to the body-fixed frame.

of the spherical harmonics. Owing to the three-fold symmetry of the potential, μ is restricted to integral multiples of 3.

The interaction potential (4.89) is expressed in the BF frame (X, Y, Z) , whereas the rotational eigenfunctions, (4.87) and (4.88), are expressed in the SF frame (x, y, z) . The relationship

$$Y_{\lambda\mu}(\theta', \phi') = \sum_{\nu} D_{\nu\mu}^{\lambda}(\alpha, \beta, \gamma) Y_{\lambda\nu}(\theta, \phi) \quad (4.90)$$

[cf. equation (4.18)] transforms the spherical harmonics in (4.89) from the BF coordinates (θ', ϕ') into the SF coordinates (θ, ϕ) , yielding $V(\alpha, \beta, \gamma, R, \theta, \phi)$. We recall that the Euler angles (α, β, γ) rotate the SF frame into the BF frame.

The total wave function describing the atom–molecule system may be expanded in terms of the functions of the total angular momentum, $\mathbf{J} = \mathbf{j} + \mathbf{l}$, where \mathbf{j} is the rotational angular momentum of the molecule and \mathbf{l} is the orbital angular momentum associated with the motion of the atom relative to the molecule:

$$|jk\epsilon JM\rangle = \langle jmlm_l | JM \rangle |jkm\epsilon\rangle |lm_l\rangle \quad (4.91)$$

In (4.91),

$$|lm_l\rangle = Y_{lm_l}(\theta, \phi)$$

and

$$\langle jmlm_l | JM \rangle = C_{mm_l M}^{jIJ}$$

is a Clebsch–Gordan coefficient; $|jkm\epsilon\rangle$ is given by equation (4.88). The total wave function

may be written in terms of the functions (4.91) as

$$\Psi(\alpha, \beta, \gamma, \mathbf{R}) = \sum_{\substack{jk \in \\ IJM}} \frac{F(jk \in IJM | R)}{R} |jk \in IJM\rangle \quad (4.92)$$

where $\mathbf{R} = (R, \theta, \phi)$ is the position vector of the He atom in the SF coordinate system.

The Schrödinger equation (4.37) must now be solved. The total hamiltonian is

$$H = h - \frac{\nabla_R^2}{2\mu} + V(\alpha, \beta, \gamma, \mathbf{R}) \quad (4.93)$$

where h is the internal rotational hamiltonian (4.85). Schrödinger's equation reduces to

$$\begin{aligned} & \left[\frac{d^2}{dR^2} - \frac{l(l+1)}{R^2} + \kappa_{jk}^2 \right] F(jk \in IJM | R) \\ & = 2\mu \sum_{j'k'\epsilon'l'} \langle jk \in IJM | V(\alpha, \beta, \gamma, \mathbf{R}) | j'k'\epsilon'l' JM \rangle F(j'k'\epsilon'l' JM | R) \end{aligned} \quad (4.94)$$

where

$$\kappa_{jk}^2 = 2\mu \left[E - \frac{j(j+1)}{2I_X} - \left(\frac{1}{2I_Z} - \frac{1}{2I_X} \right) k^2 \right] \quad (4.95)$$

and we use κ , rather than k , to denote the wave number, in order to distinguish it from the projection of \mathbf{j} on the symmetry axis of the molecule. Once again, the total angular momentum \mathbf{J} and its projection M on the SF z -axis are conserved, i.e. their values remain unchanged during the collision.

The matrix elements of the interaction potential, V , which appear on the right-hand side of (4.94) may be derived as follows. First, we substitute equation (4.88) into equation (4.91) and obtain

$$\begin{aligned} |jk \in IJM\rangle &= \langle jmlm_l | JM \rangle \\ &\times [2(1 + \delta_{k0})]^{-\frac{1}{2}} (|jkm\rangle + \epsilon |j, -km\rangle) |lm_l\rangle \\ &\equiv [2(1 + \delta_{k0})]^{-\frac{1}{2}} (|jklJM\rangle + \epsilon |j, -klJM\rangle) \end{aligned} \quad (4.96)$$

where

$$|jklJM\rangle = \langle jmlm_l | JM \rangle |jkm\rangle |lm_l\rangle \quad (4.97)$$

Second, we make use of the following relation, in terms of 3j- and 6j-coefficients,

$$\begin{aligned} & \langle jklJM | V(\alpha, \beta, \gamma, \mathbf{R}) | j'k'l' JM \rangle \\ &= \sum_{\lambda\mu} v_{\lambda\mu} (-1)^{j+j'+k'-J} \left[\frac{(2j+1)(2j'+1)(2l+1)(2l'+1)(2\lambda+1)}{4\pi} \right]^{\frac{1}{2}} \\ &\times \begin{pmatrix} l & l' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & j' & \lambda \\ k & -k' & \mu \end{pmatrix} \left\{ \begin{matrix} j' & l' & J \\ l & j & \lambda \end{matrix} \right\} \end{aligned} \quad (4.98)$$

which expresses the matrix elements of V in the basis (4.97). We note that equation (4.98) is independent of M , the projection of the total angular momentum, \mathbf{J} , on the z -axis.

The coupled equations (4.94) must be solved, subject to the appropriate physical boundary conditions, to obtain the reactance matrix, \mathbf{K} , and hence the scattering matrix, \mathbf{S} . The partial cross-sections are then derived from

$$\sigma_J(jk\epsilon \leftarrow j'k'\epsilon') = \frac{\pi}{\kappa_{j'k'}^2(2j' + 1)} \times \sum_{l,l'} (2J + 1) |T_J(jk\epsilon l, j'k'\epsilon' l')|^2 \quad (4.99)$$

where $T_J(jk\epsilon l, j'k'\epsilon' l')$ is an element of the *transmission* matrix, which is related to the \mathbf{S} matrix by

$$\mathbf{T} = \mathbf{1} - \mathbf{S} \quad (4.100)$$

The total cross-section is obtained by summing (4.99) over J .

It will be recalled that the index μ , which appears in the expansion (4.89), is restricted to integral multiples of 3, owing to the three-fold symmetry of the interaction potential about the symmetry axis of the ammonia molecule. As a consequence, the 3j-symbol

$$\begin{pmatrix} j & j' & \lambda \\ k & -k' & \mu \end{pmatrix}$$

in (4.98) restricts changes in the projection quantum number to $\Delta k = 3n$, where n is an integer. This restriction relates to the fact that ortho- and para- NH_3 may be treated as distinct species, as far as non-reactive collisions are concerned. Just as in the case of H_2 , the ortho and para forms interconvert only through proton-exchange reactions.

4.4.2 Asymmetric tops

The category of asymmetric tops comprises important interstellar molecules such as water (H_2O) and formaldehyde (H_2CO). Some polyatomic molecules, such as methanol (CH_3OH), are asymmetric tops that are close to being symmetric tops [if the internal rotation of the methyl (CH_3) relative to the hydroxyl (OH) group – the *torsional motion*, which is analogous to a vibration – is neglected].

In an asymmetric top, the three principal moments of inertia have different values, i.e. $I_X \neq I_Y \neq I_Z$, and the internal rotational hamiltonian (4.84) may be written as

$$\begin{aligned} h &= \frac{\mathbf{j}^2}{2I_X} + \left(\frac{1}{2I_Y} - \frac{1}{2I_X} \right) j_Y^2 + \left(\frac{1}{2I_Z} - \frac{1}{2I_X} \right) j_Z^2 \\ &\equiv A\mathbf{j}^2 + (B - A)j_Y^2 + (C - A)j_Z^2 \end{aligned} \quad (4.101)$$

where $A = 1/(2I_X)$, $B = 1/(2I_Y)$ and $C = 1/(2I_Z)$ are the rotational constants. It follows that

$$h|jkm\rangle = [Aj(j+1) + (C - A)k^2 + (B - A)j_Y^2]|jkm\rangle \quad (4.102)$$

where $|jkm\rangle$ is given by equation (4.87).

The term $(B - A)j_Y^2$ in the hamiltonian h determines the degree of asymmetry of the top. The step-up, j_+ , and step-down, j_- , angular momentum (ladder) operators are defined by

$$j_+ = j_X + ij_Y$$

and

$$j_- = j_X - ij_Y$$

whence

$$2ij_Y = j_+ - j_-$$

and

$$-4j_Y^2 = j_+^2 + j_-^2 - j_+j_- - j_-j_+$$

Operating on $|jkm\rangle$ with j_Y^2 , we obtain

$$\begin{aligned} j_Y^2 |jkm\rangle = & -\frac{1}{4} \left\{ [(j-k)(j+k+1)(j-k-1)(j+k+2)]^{\frac{1}{2}} |j, k+2, m\rangle \right. \\ & + [(j+k)(j-k+1)(j+k-1)(j-k+2)]^{\frac{1}{2}} |j, k-2, m\rangle \\ & \left. - 2[j(j+1) - k^2] \right\} |jkm\rangle \end{aligned} \quad (4.103)$$

and equation (4.102) becomes

$$\begin{aligned} h|jkm\rangle = & \left[\frac{(A+B)}{2} j(j+1) + \left(C - \frac{(A+B)}{2} \right) k^2 \right] |jkm\rangle \\ & + \frac{(A-B)}{4} [(j-k)(j+k+1)(j-k-1)(j+k+2)]^{\frac{1}{2}} |j, k+2, m\rangle \\ & + \frac{(A-B)}{4} [(j+k)(j-k+1)(j+k-1)(j-k+2)]^{\frac{1}{2}} |j, k-2, m\rangle \\ \equiv & \frac{(A+B)}{2} [j(j+1) - k^2] |jkm\rangle + Ck^2 |jkm\rangle \\ & + \frac{(A-B)}{4} [j(j+1) - k(k+1)]^{\frac{1}{2}} \\ & \times [j(j+1) - (k+1)(k+2)]^{\frac{1}{2}} |j, k+2, m\rangle \\ & + \frac{(A-B)}{4} [j(j+1) - k(k-1)]^{\frac{1}{2}} \\ & \times [j(j+1) - (k-1)(k-2)]^{\frac{1}{2}} |j, k-2, m\rangle \end{aligned} \quad (4.104)$$

We see from equation (4.104) that $|jkm\rangle$ is *not* an eigenfunction of h , as $|j, k \pm 2, m\rangle$ appear on the right-hand side. Put another way, the matrix of h in the basis $|jkm\rangle$ is not diagonal in k : there are off-diagonal elements involving $k \pm 2$. The relative magnitudes of the off-diagonal

and diagonal elements involving k are proportional to $(A - B)/(2C - A - B)$. We note that the off-diagonal elements vanish in the limit of the symmetric top, $A = B$, as must be the case.

The eigenenergies of the asymmetric top may be obtained by diagonalizing the hamiltonian matrix. The projection, k , is no longer a 'good' quantum number. As the off-diagonal couplings are to states with $k \pm 2$, either even or odd values of k are 'mixed' through the diagonalization procedure. In other words, the eigenfunctions of h may be written as linear combinations of the eigenfunctions of the symmetric top, $|jkm\rangle$, for given values of j and m ,

$$|j\tau m\rangle = \sum_k a_{\tau k} |jkm\rangle \quad (4.105)$$

where the sum extends over either even or odd values of k , and τ labels the asymmetric top eigenfunctions. The number of the asymmetric top eigenfunctions is the same as the number of the 'primitive' symmetric top functions of which they are composed; τ is taken to be an integer, $-j \leq \tau \leq j$, which orders the energy levels for a given value of j . In the case of a near-symmetric top, $A \approx B$, a particular value of k dominates the expansion on the right-hand side of equation (4.105), i.e. the corresponding value of $a_{\tau k} \approx 1$, whereas $a_{\tau k} \ll 1$ for all other values of k . The label τ may then be identified with the dominant value of k . In the limit of the symmetric top, $A = B$. If $A = B > C$, the top is *oblate*, whereas, if $A = B < C$, the top is *prolate*.

The first quantitative calculations for an astrophysically important asymmetric top molecule related to formaldehyde (H_2CO), in collision with He [67]. The formaldehyde molecule is shown schematically in Fig. 4.4. The atoms comprising the molecule all lie in the XZ plane, with H atoms symmetrically disposed either side of the symmetry axis, i.e. the H atoms have the same Z coordinate and their X coordinates are equal in magnitude but opposite in sign. We have already noted [equation (4.87)] that the basis functions of the asymmetric top are the normalized rotation matrix elements

$$|jkm\rangle = \left(\frac{2j+1}{8\pi^2} \right)^{\frac{1}{2}} D_{mk}^j(\alpha, \beta, \gamma)$$

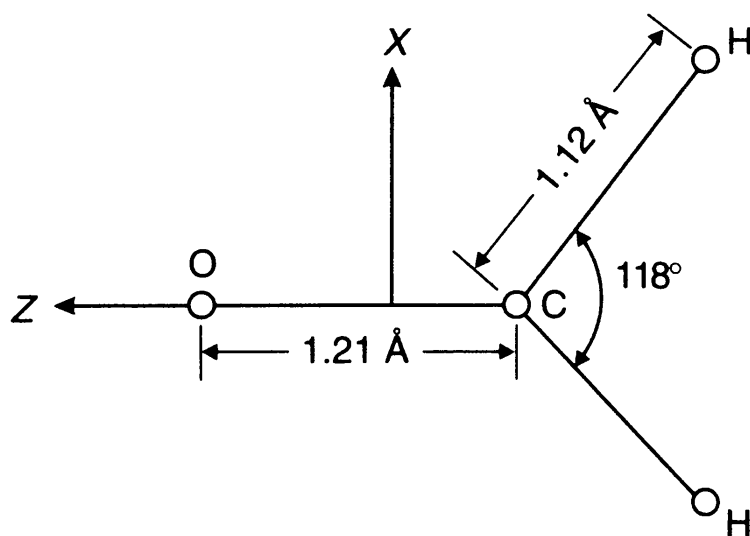


Figure 4.4 Schematic diagram of the formaldehyde molecule. The coordinate origin is located at the centre of mass of the molecule. Distances are in units of 10^{-10} m.

Exchange of the (identical) hydrogen nuclei is effected by the transformation $\gamma \rightarrow \gamma + \pi$, under which $|jkm\rangle \rightarrow \exp(ik\pi)|jkm\rangle$. Thus, if k is even, $|jkm\rangle \rightarrow |jkm\rangle$, whereas, if k is odd, $|jkm\rangle \rightarrow -|jkm\rangle$, i.e. the basis functions are symmetric or asymmetric under exchange of the H nuclei, according as k is even or odd, respectively. As the H nuclei (protons) are fermions, their total wave function, including the spin function, must be asymmetric under their exchange. The spin functions are

$$\begin{aligned} I = 1, M_I = 1 : & \quad \alpha_1 \alpha_2 \\ I = 1, M_I = 0 : & \quad (\alpha_1 \beta_2 + \alpha_2 \beta_1)/2^{\frac{1}{2}} \\ I = 1, M_I = -1 : & \quad \beta_1 \beta_2 \end{aligned}$$

and

$$I = 0, M_I = 0 : \quad (\alpha_1 \beta_2 - \alpha_2 \beta_1)/2^{\frac{1}{2}}$$

for the ortho ($I = 1$) and the para ($I = 0$) states; M_I is the corresponding projection quantum number. α denotes the proton spin state with projection $m_s = 1/2$ ('spin up') and β the state with $m_s = -1/2$ ('spin down'), and the subscripts '1' and '2' label the two protons. The ortho states are symmetric under proton exchange, i.e. under interchange of the subscripts '1' and '2', whereas the para state is asymmetric. As the total wave function is a product of the spin and the rotation parts, Fermi–Dirac statistics require that ortho-H₂CO is associated with rotational states for which k is odd only, and para-H₂CO is associated with rotational states for which k is even only. (This circumstance is similar to that in H₂, where j is odd in ortho-H₂ and even in para-H₂.) Transitions between the ortho and the para forms can be effected only by proton or hydrogen exchange reactions.

The rotational constants of formaldehyde are $A = 1.295 \text{ cm}^{-1}$, $B = 1.134 \text{ cm}^{-1}$, $C = 9.407 \text{ cm}^{-1}$, where A , B and C relate to the X , Y , and Z axes, defined in Fig. 4.4. When classifying the degree of asymmetry of tops, it is conventional to order the rotational constants such that $A > B > C$. In the example of formaldehyde, considered above, this is equivalent to a cyclic permutation of the coordinate axes, $X \rightarrow Y \rightarrow Z \rightarrow X$. The *Ray asymmetry parameter* is then defined as

$$\kappa = \frac{2B - A - C}{A - C}$$

[64]. In the limit of a prolate symmetric top ($B = C$), $\kappa = -1$, and in the limit of an oblate symmetric top ($B = A$), $\kappa = 1$. Taking the values of the rotational constants that correspond to formaldehyde, we obtain $\kappa = -0.961$, which is not far from the prolate symmetric top limit. Water (H₂O), on the other hand, for which $\kappa = -0.436$, is further from this limit.

The spectroscopic notation for the energy levels of asymmetric tops is often given in terms of the values of the projection quantum number k in the prolate and oblate symmetric top limits, k_{-1} and k_{+1} (or k_- and k_+), respectively. The index $\tau = k_{-1} - k_{+1}$ [64]. The energy levels of H₂O (para and ortho) up to 200 cm^{-1} above the ground state of para-H₂O are listed in Table 4.1. The energy levels may be labelled by j_τ or by $j_{k_-k_+}$.

Table 4.1. *Energy levels of para- and ortho-H₂O up to 200 cm⁻¹ above the ground state of para-H₂O (from [68]). The alternative methods of labelling the energy levels, by j_τ or by $j_{k_-k_+}$, are given.*

j	τ	k_-	k_+	Energy (cm ⁻¹)	modification
0	0	0	0	0.0000	para
1	-1	0	1	23.7943	ortho
1	0	1	1	37.1371	para
1	1	1	0	42.3717	ortho
2	-2	0	2	70.0907	para
2	-1	1	2	79.4963	ortho
2	0	1	1	95.1757	para
2	1	2	1	134.9018	ortho
2	2	2	0	136.1641	para
3	-3	0	3	136.7617	ortho
3	-2	1	3	142.2783	para
3	-1	1	2	173.3656	ortho

4.4.3 Asymmetric tops with internal rotation

The example that we shall take of molecules in this category is methanol (CH₃OH). Methanol is one of the most important interstellar molecules. It has been observed in many millimetre and sub-millimetre transitions, both in dark molecular clouds, where its abundance, relative to H₂, is of the order of 10⁻⁹, and in high mass protostellar objects, where its fractional abundance can reach 10⁻⁶. Methanol is both a maser (in protostellar objects) and is sometimes observed in absorption against the cosmic background (2.73 K) radiation field (in dark clouds). Grain-surface reactions are believed to be important in the production of methanol, which can be released into the gas phase by sublimation processes or by sputtering, induced by shock waves.

The richness of the spectrum of methanol reflects the complexity of its internal structure. In Fig. 4.5 is shown the equilibrium configuration of CH₃OH. The hydrogens of the methyl (CH₃) group form an equilateral triangle, as in the case of NH₃. The COH group defines a plane containing the BF Z-axis, which is perpendicular to the plane of the hydrogens and passes through the centre of mass of the molecule. The symmetry axis of the methyl group is perpendicular to the plane of the hydrogens and passes through its geometrical centre; it is parallel to, but slightly displaced from, the Z-axis.

Methanol is a slightly asymmetric top, with rotational constants $A = 0.823$ cm⁻¹, $B = 0.793$ cm⁻¹, and $C = 4.257$ cm⁻¹ along the X , Y and Z axes (cf. Fig. 4.5), respectively, in its lowest torsional state [70]. Reordering the rotational constants according to the convention that $A > B > C$, which is achieved by a cyclic permutation of the coordinate axes, $X \rightarrow Y \rightarrow Z \rightarrow X$, the Ray asymmetry parameter takes the value $\kappa = -0.983$, which is close to the prolate symmetric top limit (-1). The three protons of the CH₃ group may have 'parallel' or 'anti-parallel' spins, and these spin states can interconvert only through proton exchange reactions, just as in the case of ammonia. In A-type methanol, the total spin is $I = 3/2$, whereas, in E-type methanol, $I = 1/2$; these are equivalent to the ortho and para forms, respectively, of ammonia. The nuclear spin degeneracy, $(2I + 1)$, is 4 for A-type and

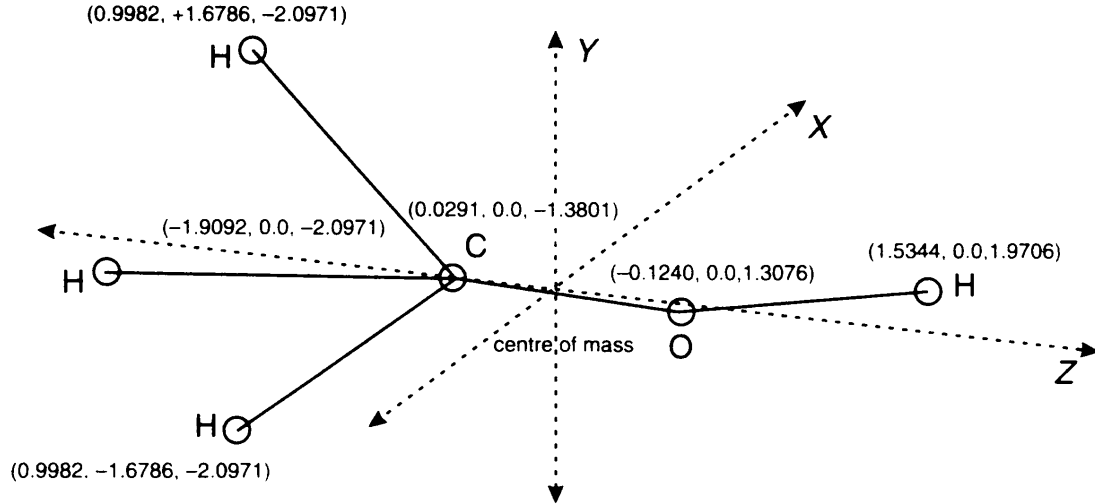


Figure 4.5 Defining the body-fixed coordinate system of methanol (CH_3OH), a near symmetric top. The (X, Y, Z) coordinates of the atoms correspond to the equilibrium configuration of the molecule [69]. Methanol exhibits internal torsional motion of the CH_3 group relative to the OH group.

2 for E-type. However, E-type methanol has two degenerate forms, E_1 and E_2 , and hence the total number of E-type states is equal to the total number of A-type states [71]. Our treatment of the internal motion of methanol closely follows that of Lin and Swalen [72]; but it should be noted that Lin and Swalen took the YZ plane to be the plane of symmetry of the molecule, whereas we adopt the XZ plane (cf. Fig. 4.5).

Let us denote the eigenfunctions of methanol by $|jk\nu\sigma\rangle$, where, as previously, j and k denote the rotational angular momentum and its projection on the symmetry (Z -) axis; ν denotes the torsional state, and $\sigma = 0$ for A-type methanol, $\sigma = 1$ for E_1 -type and $\sigma = -1$ for E_2 -type. Then the non-vanishing matrix elements of the internal hamiltonian, h , may be written

$$\begin{aligned} \langle jk\nu\sigma | h | jk\nu\sigma \rangle \\ = \frac{(A+B)}{2} [j(j+1) - k^2] + Ck^2 + E_{k\nu\sigma} \end{aligned} \quad (4.106)$$

$$\begin{aligned} \langle jk\nu\sigma | h | j, k+2, \nu'\sigma \rangle \\ = \frac{(A-B)}{4} [j(j+1) - k(k+1)]^{\frac{1}{2}} \\ \times [j(j+1) - (k+1)(k+2)]^{\frac{1}{2}} I_{k\nu\sigma}^{k+2, \nu'\sigma} \end{aligned} \quad (4.107)$$

$$\begin{aligned} \langle jk\nu\sigma | h | j, k-2, \nu'\sigma \rangle \\ = \frac{(A-B)}{4} [j(j+1) - k(k-1)]^{\frac{1}{2}} \\ \times [j(j+1) - (k-1)(k-2)]^{\frac{1}{2}} I_{k\nu\sigma}^{k-2, \nu'\sigma} \end{aligned} \quad (4.108)$$

$$\begin{aligned}
& \langle jk\nu\sigma | h | j, k+1, \nu'\sigma \rangle \\
&= \frac{D}{2} (2k+1)[j(j+1) - k(k+1)]^{\frac{1}{2}} I_{k\nu\sigma}^{k+1, \nu'\sigma}
\end{aligned} \tag{4.109}$$

and

$$\begin{aligned}
& \langle jk\nu\sigma | h | j, k-1, \nu'\sigma \rangle \\
&= \frac{D}{2} (2k+1)[j(j+1) - k(k-1)]^{\frac{1}{2}} I_{k\nu\sigma}^{k-1, \nu'\sigma}
\end{aligned} \tag{4.110}$$

$E_{k\nu\sigma} \equiv E_{-k\nu-\sigma}$ is the eigenvalue of the equation for the torsional motion, and $I_{k\nu\sigma}^{k'\nu'\sigma}$ is an overlap matrix element of the torsional eigenfunctions:

$$I_{k\nu\sigma}^{k'\nu'\sigma} = \langle k\nu\sigma | k'\nu'\sigma \rangle$$

The torsional motion is not free, but 'hindered' by a three-fold symmetric potential

$$V(\omega) = \frac{V_3}{2} (1 - \cos 3\omega) \tag{4.111}$$

where ω is the angle of rotation of the methyl, relative to the hydroxyl group; $V_3 = 373 \text{ cm}^{-1}$ is the height of the barrier to torsional motion in methanol. In the limit of an infinite barrier to torsional motion, $I_{k\nu\sigma}^{k'\nu'\sigma} = \delta_{k\nu, k'\nu'}$.

Equations (4.106–4.110) are generalizations of the previous results for the rigid asymmetric top. The additional matrix elements (4.109, 4.110) arise from the lack of rigidity of methanol, which gives rise to its torsional motion. The additional constant $D = 0.0026 \text{ cm}^{-1} \ll A, B, C$.

The energy associated with the torsional motion, $E_{k\nu\sigma}$, is much larger for A-type than for E-type methanol. As these energies appear along the diagonal of the internal hamiltonian matrix, it follows that the off-diagonal terms are smaller, relative to those on the diagonal, in A-type. In the limit of vanishingly small off-diagonal terms, the hamiltonian reduces to that of the symmetric top. This limit is approached for large j and k in both A-type and E-type, as examination of the off-diagonal terms (4.107–4.110) confirms. In the case of A-type methanol, the symmetric top limit is approached also for small j and k , and hence states $|j, \pm k, \nu, \sigma = 0\rangle$ are almost degenerate.

The eigenfunctions of the torsional hamiltonian, $|k\nu\sigma\rangle$, may be written as linear combinations of free rotor basis functions, $|km_\omega\rangle$, where m_ω denotes the torsional angular momentum of the methyl group,

$$|k\nu\sigma\rangle = \sum_{m_\omega=3s+\sigma} a_{k\nu m_\omega} |km_\omega\rangle, \tag{4.112}$$

where s is an integer and

$$|km_\omega\rangle = (2\pi)^{-\frac{1}{2}} e^{-i\rho k\omega} e^{im_\omega\omega}, \tag{4.113}$$

ρ is a dimensionless molecule-specific parameter [72], given by

$$\rho = I_\omega / I_Z,$$

where I_ω is the moment of inertia of the methyl group and I_Z is the moment of inertia of the whole molecule about the Z -axis; the numerical value appropriate to methanol is $\rho = 0.8097$ [73].

The torsional wave function, $M(\omega) \equiv |k\nu\sigma\rangle$, is the solution of the *Mathieu equation*

$$\frac{1}{\alpha} \frac{d^2 M(\omega)}{d\omega^2} + (R + 2 \cos 3\omega) M(\omega) = 0 \quad (4.114)$$

where

$$\alpha = V_3/4F$$

and

$$R = \frac{4}{V_3} \left(W - \frac{1}{2} V_3 \right)$$

$W \equiv E_{k\nu\sigma}$ is the torsional eigenenergy and F is the torsional constant. In the case of methanol, $F = 27.633 \text{ cm}^{-1}$ and $V_3 = 373.1 \text{ cm}^{-1}$ [70]. The torsional quantum number, ν , labels the different eigenvalues that have the same value of k .

In the case of $\sigma = 0$ (A-type methanol) and $k = 0$, the solutions to the Mathieu equation are analogous to the symmetrized wave functions of the simple harmonic oscillator,

$$M(\omega) = (2\pi)^{-\frac{1}{2}} \sum_{s \geq 0} (a_s e^{i3s\omega} + a_{-s} e^{-i3s\omega}), \quad (4.115)$$

in which $a_s = a_{-s}$ or $a_s = -a_{-s}$, corresponding to the torsional wave function being either symmetric or antisymmetric about the equilibrium position, $\omega = 0$, and ν being even or odd, respectively. The index ν is analogous to that used to label the eigenfunctions of the simple harmonic oscillator. The lowest energy state for a given k has the quantum number $\nu = 0$, as for the simple harmonic oscillator. In general, the solutions of the Mathieu equation have to be obtained numerically.

The lowest state of E-type methanol, ($j = 1, k = -1$), lies slightly higher (by 5.49 cm^{-1}) than the lowest state of A-type, ($j = 0 = k$). This energy difference is analogous to, although much smaller than, that between the lowest states of ortho- and para- H_2 , where the $j = 1$ ortho state is higher, by 118 cm^{-1} , than the $j = 0$ para state. Such shifts are without consequence in the context of *non*-reactive scattering, as the E/A types or para/ortho forms may be treated as distinct species that cannot interconvert. However, proton exchange reactions with ions such as H^+ and H_3^+ can interconvert these species, and the energy shifts may become significant, in this context. In the case of methanol, the energy shift is small (approximately 8 K) and has an effect on the relative abundances of E- and A-type only in very cold molecular clouds.